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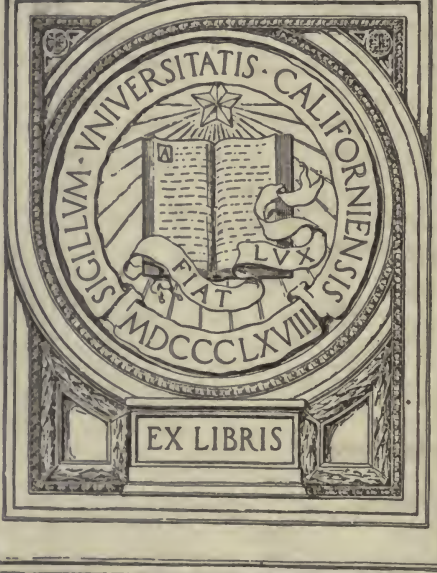

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THERMOCHEMISTRY

TEXT-BOOKS OF PHYSICAL CHEMISTRY

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THERMOCHEMISTRY

BY

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PREFACE

The experimental work, consisting of the numerical and theoretical results recorded in the following pages, was carried out in the years 1851 to 1885; the greater part of it, however, belongs to the last twenty years of that period, namely, to the time during which I held the position of Director of the Chemical Laboratory of the University. The object of the research was to undertake in as systematic and complete a manner as possible the investigation of the heat-phenomena of the more important chemical reactions, and by the interpretation of these results to gain some further knowledge as to the real nature of chemical processes.

The research as a whole, together with all the experimental details, was published during the years 1882 to 1886, in a four-volume work entitled, *Thermochemische Untersuchungen.* This work is somewhat unique, inasmuch as the author in his endeavour to solve the problems under consideration has relied exclusively upon the results of his own original, numerical determinations, which number many thousands.

The importance of these results has been in no way lessened by the passage of years, but the manner in which they have been represented and applied has often proved misleading, and more especially their authorship has frequently remained unacknowledged. It has, therefore, long been my desire to render the original results more accessible than

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was possible when the larger work, *Thermochemische Untersuchungen*, had to be consulted.

In the present volume I shall therefore review the whole of the numerical and theoretical results without devoting much space to experimental details, since these are of value only to those who intend to make a thorough study of the subject, and consequently wish to form their own opinion as to the reliance which may be placed upon the numerical values recorded, or else to those who look for guidance in the application of the same methods to new problems. It has thus been possible to reduce the size of the book to about one-fifth of that of the original work, and at the same time to provide easy access to the results themselves.

Moreover, it was also my desire that there should be a permanent record in the Danish language of the large amount of experimental work carried out at one of the scientific institutes of Denmark, the value of which will certainly be maintained as time goes on.

JULIUS THOMSEN.

COPENHAGEN,
January, 1905.

TRANSLATOR'S PREFACE

In presenting the researches of Professor Julius Thomsen to the English scientific public, the translator must call attention to the fact that since the fourth volume of *Thermochemische Untersuchungen* was published in 1886, the conception of ionization has been introduced into chemistry, and that many of the statements which Professor Thomsen has made in these pages are now generally interpreted by the light of that theory. For example, on page 123, the author has written in the Danish edition of his book: "From a general chemical standpoint, neutralization is regarded as a union of acid and base with formation of water," etc. This has been changed by the translator into: "From a general chemical standpoint, neutralization is regarded as a union of acid hydrogen and basic hydroxyl to form water," etc. In many cases, however, it has not been possible to convert the older conceptions so simply into their modern form; and the reader must remember to place the modern interpretation on the figures given should he so desire. As another example, Professor Thomsen remarks on page 154, "The avidity does not appear to be proportional to any other property of the acid," etc. It is now known that "avidity" is proportional to ionization, and is increased by dilution, and that it stands in close relationship to many other properties, such as electric conductivity and osmotic pressure. Most of the numerical relationships, however, shown

by Professor Thomsen are independent of theory, and will no doubt serve later on as a basis for some comprehensive explanation of the transferences of energy which accompany chemical reactions.

K. A. BURKE.

UNIVERSITY OF LONDON,
UNIVERSITY COLLEGE,
December, 1907.

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THERMOCHEMISTRY

INTRODUCTION

1. The Object of Thermochemical Research.

The molecular theory of chemistry as generally accepted is based upon the assumption that matter is composed of molecules, and that these again are made up of atoms. The physical condition of a body is dependent upon the arrangement and motion of the molecules, and the remaining physical and chemical properties of the substance are determined by the nature and number of the atoms in the molecule, and by their grouping and relative movements.

Every operation which produces a change in the internal structure of the molecule is a chemical process. This change may take place in various ways; it may be due to a re-arrangement of the atoms within the limits of the molecule, whereby an isomer or metamer of the original substance is formed; or to a division of the molecule into several molecules, when the process is known as a splitting up or dissociation; or it may be a union of several similar molecules, when it is known as association, condensation, or addition; or, finally, it may be the result of the interaction of dissimilar molecules, which by interchange of atoms give rise to new molecules, and this is the most frequently occurring form of chemical process.

From the law of the *conservation of matter*, it is evident that the masses of the substances which take part in a chemical process must be equal to those of the products formed; and the quantitative determination of the composition of a substance is based upon this assumption.

It also follows necessarily from the law of the *conservation*

of energy that energy can neither be destroyed nor created, and that as a consequence the total energy of the reacting substances in a chemical process will reappear in the products of the reaction, though possibly in a different form; and it is this constancy which forms the basis of quantitative thermochemistry.

The energy of a molecule is always the same at the same temperature; any increase or diminution in the energy of a molecule, without a corresponding change of internal structure, will therefore manifest itself by an increase or decrease in the temperature (or by a change in the electrical condition) of the substance in question.

When in a chemical process there is a change in the configuration of the molecules, the relative position of the atoms is altered, new relations are set up between them, and the new molecules come into being with a potential energy which may be greater or less than that of the original molecules, and this change will as a rule be manifested by a rise or fall in temperature.

The simplest relation naturally occurs on formation of isomeric or metameric substances, where the change is limited to an alteration in the relative positions of the atoms within the molecule, as a result of which the stability will be either increased or lessened. This will be accompanied by a respective rise or fall in the temperature of the substance in question, and there will therefore be a *thermal effect;* that is to say, an evolution or absorption of heat.

Similar relations hold for other chemical processes. When the molecules formed in a reaction contain a smaller amount of energy than those from which they were derived, the process will be accompanied by a rise in temperature, which will as a rule be greater in proportion to the amount of change brought about in the configuration of the molecule. If the reaction proceeds rapidly, the rise in temperature may even approach a red heat; then the process is of the nature of a combustion.

The main object of quantitative thermochemical research is the measurement of the amount of heat developed or absorbed

in chemical processes. These values do not give us any direct information as to the magnitude of the forces which influence chemical reactions, partly because they only express the difference between the energy of the original molecules and that of those subsequently formed, and partly because they are very frequently influenced by external conditions; but nevertheless they afford valuable material upon which may be based certain theoretical conclusions. Thus the principal aim of thermochemistry is the application of the laws of dynamics to chemical processes in order to increase our knowledge of chemical compounds, that is, of the constitution of molecules.

Great uncertainty still prevails as to the configuration of molecules and the true nature of atoms; all that we really know is the relative number of atoms in the molecule, their relative masses, and the existence of certain groups of atoms or radicals. But our knowledge is still extremely limited with respect to the forces which prevail in the molecules, and which lead to their formation or decomposition.

The influence of dissimilar molecules on each other is apparently independent of their masses, since it sometimes manifests itself as an attraction, sometimes as a repulsion; and moreover the power that the atoms have to combine with other atoms is limited by definite conditions (valency). But a satisfactory explanation of these important facts has not yet been discovered.

It is therefore not yet possible to extend to chemical processes that complete mathematical treatment which has been applied to the phenomena of physics and astronomy; for the essential condition for a mathematical treatment is wanting, namely, a knowledge of the fundamental laws which determine the operations of atoms. But every decade chemistry approaches more and more nearly to an exact science, and as the outcome of practical experience we can deduce many possible new laws of more or less general application. The immense amount of material available is already to some extent co-ordinated, and substances are divided into comprehensive groups, the members of which follow the same

rules or laws with respect to their formation or decomposition, and of which the properties can be partly predicted from the configuration of the molecules.

There can therefore be no doubt but that the reciprocal relations of atoms, their mutual attractions, and the very varying influences they exert on each other, in other words their *affinities*, are in accordance with the general mechanical laws of both dynamical and statical phenomena; and *the "right of the stronger" holds good in the province of chemistry as well as in that of mechanics.* It is owing to this that we can establish laws for the statics and dynamics of chemical phenomena, even although the actual nature of affinity is unknown.

2. Thermochemical Formulæ and Symbols.

A chemical reaction is usually expressed by means of an equation which represents the reacting substances as well as the products formed. But the reaction is as a rule associated with certain heat phenomena; that is to say, there is generally a difference between the energy content of the reacting substances and that of the products formed. When this difference is positive an evolution of heat takes place; on the other hand, when it is negative the products formed are at a lower temperature than were the reacting substances; in other words, a cooling effect is produced due to the absorption of heat.

The complete representation of a chemical reaction must therefore contain an additional term corresponding to the change of energy; for example

$$Cl_2 + H_2 = 2HCl + V$$
$$Zn + 2HCl = ZnCl_2 + H_2 + V',$$

where V and V' express the thermal phenomena attendant upon the process, and therefore give the number of units of heat which are liberated or bound as a result of the difference in the energy content of the original substances and of that of the products formed.

I use the words "*thermal effect*" as a general expression

for the evolution or absorption of heat attendant upon a chemical reaction; thus in the first case this value will be positive, in the second negative.

The thermal effect associated with the formation of the compound $X_aY_bZ_c$ from its constituents X_a, Y_b, and Z_c, is expressed by the formula

$$(X_a, Y_b, Z_c), \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

which contains the symbols of the elements, separated by commas, and enclosed within a bracket.

The constituents from which a compound is formed, as well as the product itself, are always assumed to be present in that state of aggregation (solid, liquid, or gaseous) in which the substances exist under ordinary conditions at a temperature of from 18° to 20°C., at which all the determinations were made. When the measurements are carried out at any other temperature this is always specially mentioned.

We may take as an example the formation of lead sulphate, $PbSO_4$. If we assume the compound to be formed from the elements lead, sulphur, and oxygen, the formula representing the thermal effect will be

$$(Pb, S, O_4);$$

on the other hand, the formulæ are respectively

$$(PbS, O_4), \quad (PbO, SO_3), \quad PbO_2, SO_2),$$

according to whether the formation of the lead sulphate takes place by the oxidation of lead sulphide, or by the combination of lead monoxide with sulphur trioxide, or by the reaction between the dioxides of lead and sulphur.

In accordance with formula (1)

$$(X_aY_b, Aq) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

represents the *heat of solution* of the substance; that is to say, the thermal effect due to the solution of the substance in water at the normal temperature of from 18° to 20°. Strictly speaking, the formula should refer to the heat of solution in an infinitely large amount of water, but it is usually given for an amount equal to from 200–400 gram-molecules of water for

each gram-molecule of the substance, and thus corresponds to the formula

$$(X_a Y_b, 200H_2O), \text{ etc.}$$

If we assume that the substance is formed in the presence of a larger amount of water, in which it subsequently dissolves, the thermal effect will be

$$(X_a, Y_b, Aq) = (X_a, Y_b) + (X_a Y_b, Aq) \quad . \quad (3)$$

In certain cases the formula

$$(X_a : Y_b) \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

is employed instead of formula (1), in order to indicate that the substances X_a and Y_b do not unite directly to form a new substance, but that they decompose each other. Thus while the formula (HgO, Cl_2) represents the thermal effect of the combination of chlorine with mercuric oxide to form an oxychloride, $(HgO : Cl_2)$ on the other hand expresses the thermal effect on formation of mercuric chloride and free oxygen. The last reaction is that which is usually known as a "*single decomposition*," and the formula will be

$$(XY : Z) = (X, Z) - (X, Y) \quad . \quad . \quad . \quad (5)$$

For instance, the thermal effect of the action of zinc upon gaseous hydrogen chloride is represented by

$$(Zn : 2HCl) = (Zn, Cl_2) - 2(H, Cl),$$

or the decomposition of an aqueous solution of copper sulphate by means of iron by

$$(CuSO_4Aq : Fe) = (Fe, SO_4Aq) - (Cu, SO_4Aq).$$

The equation for the thermal effect of a "*double decomposition*," as when XY and ZV suffer mutual decomposition with the formation of XZ and YV, is expressed by

$$(XY : ZV) = (X, Z) + (Y, V) - (X, Y) - Z, V) \quad . \quad (6)$$

as for example in the reaction between lead oxide and hydrogen sulphide

$$(PbO : H_2S) = (Pb, S) + (H_2, O) - (Pb, O) - (H_2, S).$$

Finally, I use the formula

$$(X_a Y_b Z_c) \ldots \ldots \ldots \quad (7)$$

to represent the *amount of energy associated with the molecule* $X_a Y_b Z_c$.

There are, therefore, in all *three different expressions* which are employed in thermochemical equations, namely

$$(X_a, Y_b), (X_a : Y_b), \text{ and } (X_a Y_b).$$

The *first* gives the thermal effect of the combination of the reacting constituents X_a and Y_b; the *second* the thermal effect due to the mutual decomposition of the same substances; and the *third* the amount of energy associated with the substance $X_a Y_b$.

The *thermal unit* used is the calory, that is to say, that amount of heat required to raise 1 gram of water through 1° C. when the temperature is between 18° and 20°. The *unit of weight* is the gram, since the atomic weight of oxygen is taken as 16 grams. Thus

$$(H_2, Cl_2) = 44{,}000 \text{ c}$$

indicates that 1 gram-molecule of hydrogen and 1 gram-molecule of chlorine unite to form 2 gram-molecules of *HCl*, or 73 grams of hydrogen chloride, with an evolution of 44,000 calories; whilst

$$(N_2, O_2) = -43{,}150 \text{ c}$$

signifies that the formation of 2 gram-molecules, or 60 grams, of nitric oxide from nitrogen and oxygen is attended by an absorption of 43,150 calories.

3. Thermochemical Principles.

Some of the main propositions upon which thermochemical researches are based can be derived *à priori* from the law of the conservation of energy. In 1853 and the following years I published a number of papers in Poggendorff's *Annalen der Physik und Chemie*, in which I drew attention to certain of these conclusions, and pointed out their significance in the interpretation of the results of thermochemical experiments.

I laid especial stress upon the following laws, which we shall frequently have occasion to use :—

The magnitude of the thermal effect on formation of a chemical compound is equal to the difference between the sum of the energy content of the reacting substances and that of the compound formed. This is expressed by the equation

$$(P, Q) = (P) + (Q) - (PQ) \quad . \quad . \quad . \quad (8)$$

in which (P), (Q), and (PQ) represent respectively the amounts of energy associated with the constituents and with the compound itself. Hence it follows that—

When the sum of the energy content of the reacting substances is greater than that of the compound formed, the process will be attended by an evolution of heat; in the opposite case an absorption of heat will ensue.

From the reverse equation

$$(P, Q) = -(P) - (Q) + (PQ)$$

it follows that the *thermal effect on the decomposition of a compound into its constituents is equal in value, but opposite in sign, to that which occurs on formation of the compound from the same constituents.*

Furthermore, it is evident from the law of the conservation of energy that : *When a group of substances pass through a series of successive chemical reactions of such a nature that the final products are identical with those originally present, the sum of the thermal effects of the combined processes will be equal to zero, provided always that no external source of energy is allowed to influence the system.* Thus if we suppose that in the first instance the substances P, Q, R, and S unite directly to form $PQRS$, and that this compound is then split up into PQ and RS, and that these new compounds are finally again resolved into their original constituents, we shall then have

$$(P, Q, R, S) - (PQ, RS) - (P, Q) - (R, S) = 0,$$

from which we can derive the equation

$$(P, Q, R, S) = (P, Q) + (R, S) + (PQ, RS) . \quad (9)$$

and this may be expressed as follows :—

The thermal effect due to the formation of a compound from the same constituents has always the same value, no matter whether the compound is formed directly or by successive stages; or more generally, *when the same products are formed from the same constituents in a variety of ways, but without the agency of any source of external energy, the total thermal effect will always be the same, and its magnitude is dependent only upon the condition in which the reacting substances exist at the beginning and end of the course of reactions.*

The preceding law is of considerable importance in thermochemical research, and has been extensively used in settling the thermal effect of a number of chemical processes; as, for example, the heats of formation of the majority of organic substances.

The collective results of my researches are divided into four main divisions. *Part I.* contains the results of determinations of the thermal effect on formation of aqueous solutions, together with an account of their properties. The contents of the seven chapters include the heats of solution, and their dependence upon the amount of water; partial decomposition in aqueous solution; and dependence of the thermal effect upon the temperatures and specific heats of the liquids, based on an investigation of the specific heats of the solutions.

In *Part II.* are given the results of determinations of the thermal effect on formation of compounds composed of non-metals only.

Part III. deals with the investigation of the compounds between metals and non-metals; that is, with the formation of the oxides, hydroxides, sulphides, salts, etc.

Finally, in *Part IV.* will be found an account of the thermochemistry of organic substances. Each Part will contain a chapter dealing with the subject from the theoretical standpoint.

EXPERIMENTAL CALORIMETRIC METHODS

I. Description of the Method.[1]

The majority of organic substances cannot be formed directly from their elements in a manner suitable to the quantitative determination of their heats of formation. An alternative method must therefore usually be adopted for calorimetric purposes, and, as described in the opening paragraphs of Chapter XIII., it is generally possible to determine the heats of formation indirectly from a knowledge of the heat of combustion of the substance and of the heats of formation of the products of its decomposition. If, for instance, the molecular formula of the substance which has undergone combustion is $C_aH_{2b}O_c$, the heat of combustion will correspond to (C_a, H_{2b}, O_c).

To express the heat of combustion I make use of an abbreviated formula, writing

$$\int(C_aH_{2b}O_c) \textit{ for } (C_aH_{2b}O_c,\ O_{2a+b-c}).$$

We then have the equation

$$(C_a, H_{2b}, O_c) + \int C_aH_{2b}O_c = a(C, O_2) + b(H_2, O).$$

That is to say, from the elements a atoms of carbon, $2b$ atoms of hydrogen, and c atoms of oxygen, we have formed on the one hand $C_aH_{2b}O_c$, which is oxidized by the rest of the oxygen into a molecules of carbon dioxide and b molecules of water (see left-hand side of the equation); on the other hand, the a atoms of carbon and the $2b$ atoms of hydrogen are converted by means of the $2a+b$ atoms of oxygen into a molecules of carbon dioxide and b molecules of water (see right-hand side of the equation).

The total amount of heat should be the same in the two cases, since the same products are formed from the same elements, so that the heat of formation of the combination is

$$(C_a, H_{2b}, O_c) = a(C, O_2) + b(H_2, O) - \int.C_aH_{2b}O_c.$$

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[1] *Note by Translator.*—The experimental details contained in this chapter are abstracted from *Thermochemische Untersuchungen*, vol. iv., and do not form part of the Danish work, *Thermokemiske Resultater*, of which the rest of the book is a translation.

The heat of combustion of organic bodies, apart from its technical importance, is not in itself of any special interest, since it represents the sum of the thermal effects of a number of phenomena, and does not furnish us with any insight into the nature of the substances. We can, it is true, trace certain relationships between the heats of combustion and the other properties of the bodies in question, but these are not of any particular value, since the heats of combustion of the constituents exercise a very great influence upon that of the body itself; whilst the characteristic thermal property of each body (that is to say, the heat of formation, sometimes positive, sometimes negative) is relatively much smaller, and, in comparison with the other properties of which we shall have to speak, frequently does not manifest itself in a sufficiently definite manner.

Nevertheless, a knowledge of the heats of combustion of substances is of fundamental importance in thermochemical research, since by means of this and of certain other values, namely, the heats of combustion of the constituent elements, the capacity for heat, and the latent heat of the body and of its constituents, etc., we can calculate the heat of formation. It is easy to see that the value of the heat of formation will vary somewhat according to which of the specified values be selected for the calculation; but in any case the data furnished by the experimental determinations of the heats of combustion are always available, and by means of this fundamental value different experimenters can determine the heat of formation itself, by making use of such supplementary data as seem to them the most accurate.

It is self-evident that the heat of formation of a body will be different according to whether it is given for the body in the solid, liquid, or gaseous state; it is therefore advisable that when comparing the heats of formation the substances should always be in the same physical condition, and the gaseous state has been found most suitable for this purpose. I have consequently based my researches upon an examination of volatile organic substances, and in every experiment have measured the heat of combustion *directly in the state of gas or vapour.*

Amongst the immense number of organic compounds actually known to us, it was obviously necessary to restrict the experimental researches within somewhat narrow limits, in order that the data obtained might bear some relation to each other, and not consist only of a number of isolated examples. I therefore decided to study a few of the most important groups of substances as completely as possible, so that the conclusions drawn from the results might have a greater theoretical value, rather than to undertake an investigation of the reactions of a number of substances differing widely in constitution.

The choice of material was determined by the following conditions: First of all, could the body be obtained in a sufficiently pure state? secondly, was it a gas, or had it a boiling-point low enough for practical purposes? and finally, did the body belong to a group of substances of any theoretical importance? About 120 organic compounds were eventually selected for investigation; these substances belong to the following groups: *hydrocarbons; chlorine, bromine, and iodine compounds; alcohols; acids; aldehydes; ketones; oxides of alcohol radicals; sulphur compounds; esters; amines; nitrogen compounds and substances related to them.*

I usually studied the first member of each series, and, when possible, some of its homologues. In the substances studied the number of atoms of carbon in the molecule was rarely greater than six; in the aromatic compounds, however, substances containing as many as nine atoms of carbon in the molecule were studied, since the first member already contains six. The reason for this limitation is that compounds containing a large number of carbon atoms have very large heats of combustion, and as the percentage error in combustion experiments is always about the same, the actual numerical accuracy of the heats of combustion will vary according to the number of carbon atoms. Now the calculation of the heats of formation are based upon the values found for the heats of combustion; hence the former magnitudes will be greatly influenced by the total numerical error of the latter. And as each new atom of carbon that enters into the molecule in a

series of homologous compounds increases the heat of combustion about twenty-five times as much as it does the heat of formation, the numerical error of this last value, when calculated in the manner mentioned above, will vary very considerably with the amount of carbon in the molecule. With a molecule containing eight atoms of carbon the heat of combustion will be of the order of a million units, and a possible error of $\frac{1}{4}$ per cent. in this value will occasion a variation of some thousands of units in the heat of formation. Combustion experiments are therefore not adapted to the study of the thermal properties of substances containing a large number of carbon atoms in the molecule, nor is there any other method known which is suited to the purpose; but for the first members of each series a measure of the heats of combustion provides most valuable data; moreover, the experiments can be very easily carried out, and the products of combustion are all well-known substances, such as water, carbon dioxide, etc.

My researches were consequently confined to volatile organic compounds, the heats of formation of which were almost exclusively deduced from their heats of combustion.

II. Description of the Apparatus.

1. Method of obtaining a Steady Combustion.

The apparatus employed in the measurement of the heats of combustion is practically independent of the nature of the substances to be studied. The method is reduced to its simplest form *when dealing with gases*, for in this case the dry gas is collected over mercury in a gasometer, and then led with a regulated velocity into the calorimeter where it is burned in oxygen.

If the gas has a high percentage of carbon, and burns with a smoky flame, it is necessary to dilute it in the gasometer; for this purpose we make use, according to the conditions, of nitrogen, or atmospheric air, or of air mixed with varying proportions of oxygen, in such a manner that the quantity of oxygen introduced into the mixed gases amounts to from 40 to 50 per cent. of the total volume.

In this manner we can obtain a gaseous mixture in which the substance burns completely in the oxygen in the calorimeter, and without the production of soot or the deposition of graphite in the orifice of the burner.

The oxygen used in the combustions is stored in a dry gas-holder, and is led with a regulated and constant velocity into the calorimeter, where combustion takes place under atmospheric pressure; any irregularities are eliminated by means of certain arrangements which will subsequently be described (see below).

The gases issuing from the calorimeter contain different products according to the composition of the substance under examination; when the latter contains only carbon, hydrogen, and oxygen, the products consist solely of carbon dioxide and water, mixed with the excess of oxygen, for the passage of the gases through the calorimeter is so arranged that about half of the total amount of oxygen is found in excess at the exit of the calorimeter.

In nearly all the combustions a small quantity of nitric acid is formed at the expense either of the air contained in the apparatus at the beginning of the experiment, or of the air which had been mixed with the gas. The nitric acid formed becomes more important when the substance itself contains nitrogen, as, for example, the amines and nitriles; and it is formed in even greater quantity when the nitrogen of the compound is present in direct combination with oxygen, as in the case of nitroso-compounds, and the nitrites and nitrates of alcohol radicals. In the last case especial account must be taken of it, but otherwise the quantity of nitric oxide formed, which unites with the water and oxygen to form nitric acid and then dissolves in the water, is too small to influence sensibly the heat of combustion.

The gases which come off are passed through a U-tube containing sulphuric and chromic acids, by means of which the last traces of nitric oxide are removed before the gases arrive at the apparatus where the carbon dioxide is absorbed.

I satisfied myself by a special series of preliminary experiments that under the conditions employed the combustion

is as complete as possible, and that any secondary products, such as carbon monoxide, that might be formed are so minute in quantity that their influence may be neglected in calculating the heats of combustion. In any case, the apparatus necessary for the determination of these products would introduce considerable complications, and would lead only to a very uncertain correction, or at any rate to one falling within the limits of errors of observation, and, what is more, obtained at the expense of the accuracy of the calorimetric measurements. I have, therefore, in every case assumed the combustion to be complete, and have calculated the thermal values on this supposition.

An absolutely regular rate of combustion is obtained by eliminating all variations of atmosphere pressure during the course of the experiment, which is easily accomplished by the following arrangement. The gases, oxygen and substance to be burnt, flow through the calorimeter with a constant velocity, which, when once established, does not change. Just before the entrance to the calorimeter the gases pass through a region tightly packed with capillary tubing; this produces a sufficient difference between the internal and external pressure in the space where the combustion takes place to render any stoppage or back-flow of the current of gas impossible, and the fluctuations are reduced to a minimum. The products of combustion issuing from the calorimeter must also pass through a constricted portion of the circuit before arriving at the absorption apparatus. A Liebig's potash bulb is used to absorb the two to four grams of carbon dioxide resulting from the combustion, and the use of this apparatus produces continual oscillations of pressure.

These oscillations are completely eliminated by sending the gases through another constricted portion of the circuit before they arrive at the potash bulbs. The U-tubes for the absorption of the nitric oxide and water vapour are placed between these two constricted areas, so that the space within these tubes forms a sort of reservoir, by means of which the oscillations of the current of gas are equalized, and a water manometer connecting this part of the circuit to the exit tube of

the combustion chamber does not show any variations of pressure.

The gases issuing from the absorption tubes reach an aspirator, where the pressure is kept constant, and so regulated that the water-manometer in the circuit indicates a constant depression of about 1 cm. The combustion therefore takes place under the same conditions as would exist in a free atmosphere rich in oxygen.

When the substance under examination is not a gas, a "universal burner" is used, in which it is burnt in the state of vapour. With a substance of low boiling-point, containing two or three atoms of carbon and a large number of hydrogen atoms in the molecule, it is possible to carry out the experiment at the boiling-point of the liquid. If, on the contrary, the substance has a high boiling-point, or is rich in carbon, it is diluted with air as it arrives above the jet of the universal burner; in this manner the temperature is reduced, and the vapour reaches the calorimeter at a temperature below the boiling-point. In such a case, to ensure a steady combustion, it is necessary to have an additional constriction in the circuit, and to reduce the size of the platinum tube which forms the orifice of the burner. In other respects the combustion is carried out as in the case of gases, only that special care must be taken to regulate the flame of the burner before starting an experiment, in order to avoid any irregularities.

2. Calorimeter.

The calorimeter used in the experiments described is represented in Fig. 1. The interior is of platinum, and consists of a combustion chamber, *a*, of 200 c.c. capacity, surrounded by a spiral tube, *cc*, 1·8 metres long and 5 mm. in diameter, through which the gases pass to the absorption tubes. At the bottom of the combustion chamber is an opening, *g*, into which a conical platinum tube is soldered. This tube serves to support the combustion chamber within the outer chamber of the calorimeter, through the floor of which it is soldered. The universal burner, which will

subsequently be described, is inserted into the opening *g*, and is connected up with the tubes conveying the oxygen and the substance about to undergo combustion.

The calorimeter chamber, A, which has a capacity of about 3 litres (in some of the earlier experiments a similar apparatus of only 2 litres capacity was used), is made of brass, and is supported upon three points fixed to a tripod stand; it is closed at the top by means of an ebonite cover, *e*. *It was not considered necessary to surround the calorimeter with a series of external jackets*, since it was possible to arrange so that the temperature of the laboratory, where the experiments were carried out, did not vary by more than one-tenth of a degree during the course of several hours. The calorimeter thus stands free in the air, and is simply protected by an ebonite cylinder, *d*, open at each end, from any possible radiation from the person of the experimenter. This screen is supported upon three points, and in no way interferes with the free circulation of the air around the calorimeter.

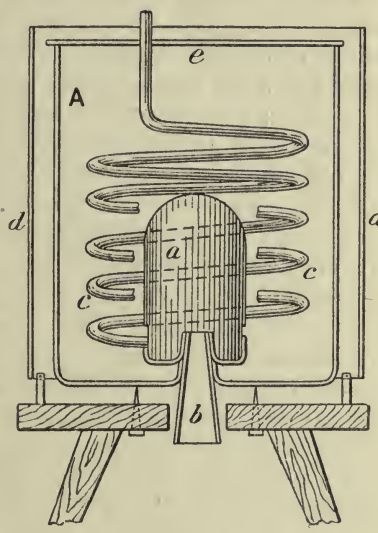


FIG. 1.

The water in the calorimeter is kept in continual motion by means of a circular stirrer passing between the walls of the combustion chamber and the spiral tube; the stirrer is worked by a small motor, which is represented in Fig. 5, E.

There are four openings in the ebonite cover of the calorimeter, one for the thermometer, another for the spiral tube, whilst the other two serve for the passage of the wires in connection with the stirring apparatus.

3. Apparatus for supplying the Oxygen.

The oxygen required for the combustion is led into the calorimeter from the apparatus represented in Fig. 5. This is so arranged that the oxygen arrives at the calorimeter with a regular velocity, which is independent of the level of the water in the gas holders A and B. The velocity is determined by the position of the reservoir A, which is therefore placed at the height necessary to ensure the requisite supply of oxygen; and, once this velocity has been established, the gasometer will always provide the same amount of oxygen in the same time. The manipulation of this gasometer has been arranged in such a manner that it is never necessary to alter its position, no matter whether it empties itself or whether it has to be refilled with gas.

Before passing into the gasometer, the oxygen, prepared from potassium chlorate, is purified by means of a concentrated solution of potash; it is therefore quite dry on arriving at the calorimeter. It has already been stated that in its passage through the tubes leading to the calorimeter the oxygen is obliged to pass through a capillary tube or a cotton-wool plug in order to eliminate any variations of pressure.

4. Apparatus for supplying the Gas.

Whilst the oxygen is collected over water, a mercury gasometer is used for storing the gas about to undergo combustion. This apparatus is represented in Fig. 5, and consists of two jars, C and D; the former contains the gas under examination, which is displaced by means of the mercury in D. C has a capacity of about 3 litres; D, on the other hand, contains only 1 litre, since it is rare that more than a litre of gas is required for each experiment. It is essential that this part of the apparatus be arranged so that the gas will flow out with a velocity which remains constant during the course of an experiment, and, moreover, it must be adjustable for the different gases used.

This constant flow is obtained by arranging the jar D as

a Mariotte's flask. The air necessary to replace the mercury which flows out enters by the tube *b*, which passes down almost to the bottom of the jar. In order, as far as possible, to avoid any bumping of the mercury, due to the passage of the gas, a narrow lateral opening is made at the lower end of the tube; and, in addition, the external opening is drawn out to a fine point, so that the air enters very slowly, and only very small bubbles of air are formed as the mercury flows out. The apparatus thus formed acts just as satisfactorily as if it were filled with water.

It is possible to adjust the rate of flow by connecting the metal tap *c*, by means of a piece of indiarubber tubing, with one or other of the glass tubes *d*. These tubes vary in diameter, and allow the passage of from 0·5 to 1 litre of mercury in ten minutes when the tube *b* is fixed to the jar. Thus for each special experiment that tube is chosen which lets through the requisite amount of mercury in the time.

The mercury from D flows into the tube *e*, open at its upper end, which is in connection with the gas-holder C, and the rise in pressure is recorded by the mercury manometer *k*. If now the taps *g* and *h* are open, and the tap *i* is closed, the gas will necessarily pass out through *g* and *h*. It is possible by means of the tap *h* to set up a resistance sufficient to produce an excess of pressure, of, for example, 2 centimetres, in the gas-holder, and this remains constant as long as the motion of the mercury continues. When the experiment is finished, the taps *c* and *g* are turned off, but *h* is not touched. The apparatus is then ready for another experiment, since as soon as *c* and *g* are opened, the flow of gas is brought about by means of the excess pressure described above.

To fill the reservoir with gas, the taps *i* and *l* are opened, when the mercury flows out of *l* and the gas enters through *i*.

5. Universal Burner for Volatile Organic Substances.

By means of the universal burner it is possible to bring about the combustion of almost all volatile organic compounds of which the boiling-point is not too high, and this is

effected either at the boiling-point or at a lower temperature; in the latter case the substance is volatilized at a suitable temperature by means of a current of gas. As, for this purpose, either ordinary air, or varying quantities of oxygen and nitrogen, or hydrogen may be used, it is possible thus to effect the combustion both of those substances which under ordinary conditions give rise to smoky flames, and which when burnt in an atmosphere of oxygen tend to block up the orifice of the burner with graphite, as well as of those substances which are not themselves combustible; as, for example, many chlorine derivatives, such as the chlorides of carbon, chloroform, etc., and of which a complete combustion can only be brought about by means of the universal burner.

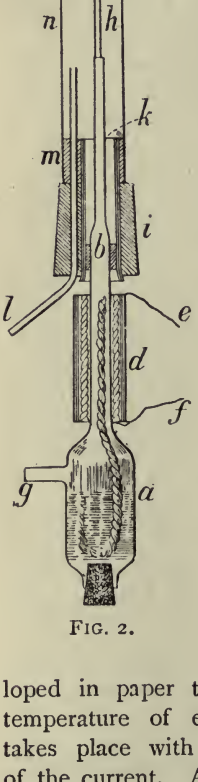


FIG. 2.

In Fig. 2 the universal burner is represented in half scale. The liquid to be burnt is placed in the small bulb *a*, and passes up by means of a wick of purified cotton or asbestos into the tube *b*, in connection with *a*, where it is heated. The tube *b* is surrounded by a larger glass tube, *d*, and between these two tubes there is a spiral of fine platinum wire, the extremities of which are represented in the diagram by the letters *e* and *f*. By passing an electric current through this spiral, the wick can be raised to any desired temperature. The tube *d* is enveloped in paper to prevent too rapid cooling. When the temperature of ebullition has been reached, vaporization takes place with a velocity dependent upon the intensity of the current. As long as a regular current is maintained, the evolution of vapour remains constant, and the size of the flame does not vary at *h*. There is a regulator in the circuit, by means of which the flame can be brought to

the requisite size, after which it does not undergo any variation throughout the course of an experiment. In order to prevent any condensation of the vapour in its passage from *b* to *h*, a double wire of silver is introduced into the tube *h*. This tube, which is formed of a piece of platinum foil, becomes strongly heated, and communicates heat to the silver wire throughout the whole of its length from *h* to *b*. This prevents the vapour from becoming cooled, and at the same time does not produce any modification in the quantity of heat supplied to the calorimeter.

If a current of gas is to be used to volatilize the substance, either for the purpose of forming a vapour of suitable density for the combustion, or else to effect its combustion by mixing with hydrogen, the gas is introduced through the opening *g* of the lower bulb. The rate of flow of the gas, and the intensity of the electric current, must then be regulated until the flame is of the requisite size, and burns without smoke or the deposition of graphite in the orifice. To do this a preliminary experiment is made in which the burner is placed in a glass vessel, open below, and connected with an aspirator, so that the combustion takes place under the same conditions as in the actual experiments within the combustion chamber of the calorimeter. Once regulated, no variations should occur during the course of a combustion, so long as the gas-flow and the electric current are kept constant. The temperature will naturally be lower than the boiling-point of the liquid, and as this lowering of temperature has to be taken into consideration, I shall refer to it again later on.

The universal burner is connected to the calorimeter in the following manner. In the indiarubber cork *i*, which closes the aperture *g* of the calorimeter, there is a short glass tube, *k*, the internal diameter of which is about 3·2 mm. larger than that of the tube *b*. Between these two tubes there is a ring of indiarubber which joins them firmly together. The air space between these two tubes, *k* and *b*, which is filled with glass wool, helps to insulate the heat of the tube *b*. The end of the combustion tube *h* is made of platinum foil, soldered into the tube *b*.

The tube *l*, through which the oxygen required for the combustion passes, is inserted through the rubber cork *i* outside the tube *k*. The upper part of this tube is surrounded by a larger tube, closed at the top in order to distribute the current of oxygen more uniformly.

Next to the indiarubber stopper is a disc of cork, *m*, of somewhat smaller diameter, which serves to support a tube, *n*, made of platinum foil. This platinum tube surrounds the two tubes through which enter the oxygen and the vapour to be burnt; its object is to render the oxidation more effectual, and for this purpose it is filled with glass wool up to the lower part of *k*. The current of oxygen is regulated in such a manner that the products of combustion on issuing are mixed with about 50 per cent. of free oxygen.

6. Absorption Apparatus.

It is essential that the absorption tubes should have a fairly large capacity, since during the ten to fifteen minutes that an experiment lasts some 2 to 4 grams of carbon dioxide have to be absorbed, and, in addition, the excess of oxygen, amounting to about 2 litres, must pass through the apparatus.

When the combustible body does not contain chlorine, bromine, iodine, or sulphur, the products of combustion pass first of all through one or two U-tubes (Fig. 5, *3*) filled with pumice-stone saturated with sulphuric acid ($H_2SO_4 + 2H_2O$) and chromic acid, which retain the traces of oxides of nitrogen always formed. In the case of non-nitrogenous substances these oxides can only arise from nitrogen mixed with the oxygen, and are formed in very small quantity, but when the substance itself contains nitrogen the amount of oxides formed is increased. The greater part, however, condenses with the water-vapour in the combustion chamber, and must be allowed for in the calculation.

The current of gas, freed from oxides of nitrogen, passes into a drying apparatus, also composed of two U-tubes (Fig. 5,

4 and *5*); the first of these contains calcium chloride, the second pumice and concentrated sulphuric acid.

For the absorption of the carbon dioxide, a Liebig's potash bulb and two **U**-tubes containing solid potash (Fig. 5, *6*, *7*, and *8*) are used. The potash bulb, represented in Fig. 3, consists of four lower bulbs of equal size, which are connected by narrow tubes in order to render the absorption more efficient, and, in addition, there is a bulb on the inlet tube and two enlargements on the outlet tube. A 40 per cent. solution of potash is used, prepared by dissolving two parts of solid potash in three parts of water. Fifty grams of the solution are placed in the bulbs, and this is sufficient to absorb 7 to 8 grams of carbon dioxide—that is to say, two or three times as much as is produced in an experiment — and the apparatus should be recharged with alkali each time it is used. The energetic absorption which takes place heats up the potash bulb, and, as a consequence, the issuing gas is saturated with aqueous vapour. To prevent the deposition of this moisture within the tube *a* (Fig. 3), a roll of filter-paper is inserted, which absorbs any liquid that might be carried over.

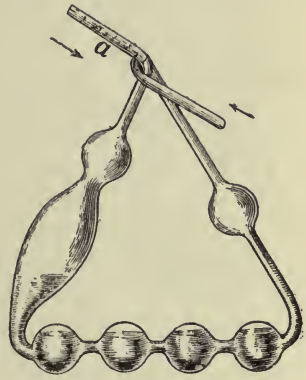


FIG. 3.

The gas which issues from the Liebig's bulb is next dried over solid potash. The amount of water which has to be absorbed in these potash tubes will naturally vary with the temperature of the potash solution in the Liebig's bulb, and also with the quantity of gas which passes through during the course of an experiment and in the fifteen minutes following the termination of the combustion. The increase in weight of the first tube varies ordinarily between 0·08 and 0·15 gram; but the second tube, even when there has been an absorption of from 3 to 4 grams of carbon dioxide in the Liebig's bulb,

does not increase in weight by more than 0·002 gram, which testifies to the completeness of the absorption. To ensure this efficient absorption in the first potash tube, and to avoid the necessity of frequently having to recharge the tube, it is filled in the following manner. The branch of the U-tube directly connected with the Liebig's bulb is filled from *a* to *b* (Fig. 4) with large lumps of solid potash; the lower part of this limb, and also the greater part of the other, from *b* to *c*, contains grains of 2 mm. diameter; and finally, from *c* to *d*, the grains are only 1 mm. in diameter. Potash of the requisite dimensions is obtained by powdering up a large quantity and then sifting it through two iron sieves with meshes of appropriate size. The gas passing through the tube deposits a large amount of moisture upon the first layer of potash; if this were not composed of fairly large lumps the absorption of water would occasion a block in the tube after some two or three experiments, whilst the larger grains merely take up moisture upon the surface and do not deliquesce until they have been in use for some time. It is therefore only necessary to refill the tube when the larger pieces of potash have become liquefied and tend to obstruct the passage of the gas. The greater portion of the moisture is absorbed close to this part of the tube, which is apparent from the fact that in the rest of the tube, with the exception of a small layer just below the larger lumps, there is no sign of any adherence between the grains, which can, on the contrary, be shaken about in the tube. Small pieces of cotton-wool are placed between the different layers, and at the top of the layer of finely powdered potash there is a plug of wool pressed tightly in for the purpose of filtering the gas. The second tube is filled with grains of potash of about 2 mm. diameter; this rarely requires to be renewed, since the amount of water absorbed in a hundred experiments is only a few decigrams.

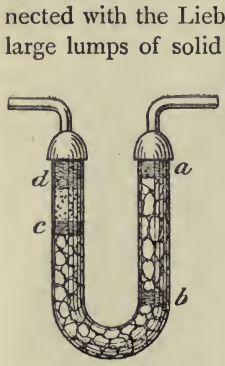


FIG. 4.

When the substance contains elements other than carbon,

hydrogen, oxygen, and nitrogen, as, for example, chlorine, bromine, iodine, or sulphur, special absorption apparatus is required in addition to that already mentioned, and this will be described later on.

7. Aspirator.

The absorption apparatus just described, together with the constricted areas introduced into the circuit with a view of eliminating the variations of pressure occasioned by the absorption, produces a certain resistance, which is overcome by means of an aspirator.

Like all the other parts of the apparatus, the aspirator is arranged in a manner that makes it easy to set up a small difference of pressure, and to maintain this pressure constant throughout the course of an experiment. This result is obtained by means of a Mariotte's flask, in which the rate of flow from the outlet tube can be controlled.

The aspirator is represented in Fig. 5, G. The tube *a* conveying the gas passes into a flask of about 6 litres capacity. This tube, which can be closed by a tap, reaches to the bottom of the jar. Into the lateral aperture, closed by a tap, *b*, through which the water flows out of the aspirator, is fixed a vertical tube, *c*, of 0·5 metre in length and surrounded by another tube, *d*, closed below, so that the water issuing from the gas-jar cannot flow out directly, but must first pass up throughout the whole length of *d* before it can escape. The actual pressure in the aspirator depends only upon the difference in level between the lower end of the tube *a* and the exit of *d*; this latter is controlled by a weight, and can consequently be raised or lowered until the necessary pressure is obtained. A comparison of the volume of gas passing into the aspirator with that issuing from the gasometer affords a means of ascertaining whether the combustion is proceeding with a continuous excess of oxygen, since this is the case when about half of the oxygen passing into the calorimeter reaches the aspirator unabsorbed.

8. Description of a Calorimetric Experiment.

The apparatus employed in a calorimetric experiment is represented in Fig. 5. The mode of procedure is as follows: AB is the apparatus for supplying the oxygen; when the taps *a*, *b*, and *c* are open, and *d* is shut, the gas flows out of B with a constant velocity. The three-way tap *a* is so arranged that the oxygen passes through the drying tubes 1 and 2, the first of which contains sulphuric acid, the second caustic potash. The water which displaces the oxygen flows from A into B by means of a tube having a tap, *b*, while the atmospheric air enters the reservoir by the tap *c*. As a result of preliminary experiments, the rate with which the oxygen will flow out when A is raised to a definite height is known; and it is possible to regulate the position so as to obtain the requisite amount of oxygen per minute. As the tube through which the oxygen passes to the burner is constricted close to F, *a*, in order to diminish variations of atmospheric pressure, the oxygen in B always has a small excess pressure, which varies from 10 to 20 cm., according to the height of A.

CD is the mercury gasometer for storing the gas under examination. When the taps *l*, *m*, and *i* are open, and the others closed, the mercury will flow out of C and will be replaced by the gas required, which, previously purified and dried, passes in through the tap *i*. If the gas contains more than one atom of carbon in the molecule it is diluted with dry atmospheric air, freed from carbon dioxide, or else with air mixed with oxygen, in order that the combustion may take place without deposition of soot. When the taps *l* and *i* are shut, and *c*, *f*, *g*, *h*, *k*, and *m* are open, the mercury flows with a constant velocity by means of the tube *e* from D into C, displacing the gas, which passes by way of *g* and *h* to the burner. The velocity of the gas current is regulated by the tube *d* fixed to the tap *c*, that tube being chosen which lets through the amount of mercury necessary to produce a gas current of the required strength. By turning the tap *h*, a resistance can be offered to the gas so that there is an excess of pressure in C corresponding to 2 or 3 cm. of mercury; this pressure is

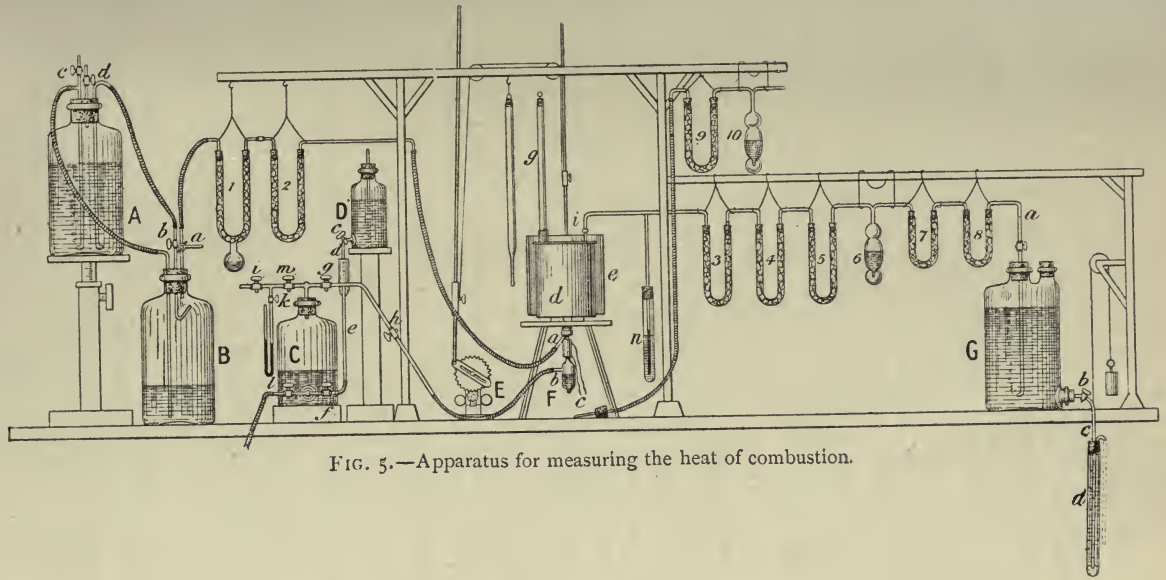


FIG. 5.—Apparatus for measuring the heat of combustion.

registered on the manometer *k*. The velocity of the current of gas is not modified by this pressure, but is determined by the quantity of mercury flowing out of D in a minute, and is exempt from any variations. After the apparatus has been set up ready for use the taps *c* and *g* are closed; then, when a combustion is to be performed, it is only necessary to open these taps to obtain a current of gas of the strength previously arranged for, and which will remain constant throughout the course of the experiment.

F represents the calorimeter and its accessories, with the universal burner and its connections, *a*, *b*, and *c*; *d* is the calorimeter proper, of about 3 litres capacity, surrounded by a circular screen of ebonite, *e*, and covered by a lid of the same material. (In the diagram this screen is represented in section.) A thermometer, *g*, is fixed through the lid, and a similar thermometer is suspended by the side of the calorimeter to register the temperature of the surrounding air. The stirrer passes in through *f*; it is moved up and down by means of a motor, E. The gas or vapour to be burnt, and also the oxygen required, enter the calorimeter by way of the universal burner, while the gaseous products of the combustion issue through the opening *i* of the platinum spiral of the calorimeter and pass on to the absorption tubes.

When the combustible substance contains only carbon, hydrogen, and nitrogen, tube *3* contains a mixture of sulphuric and chromic acids, tube *4* calcium chloride, and tube *5* concentrated sulphuric acid (these three tubes are for the purpose of retaining aqueous vapour and oxides of nitrogen), *6* is the Liebig's bulb, containing a 40 per cent. solution of alkali, and *7* and *8* are the tubes for the solid potash. The gases then pass into the aspirator. When the aspirator taps are open, the gas is drawn through the absorption tubes exposed to a constant pressure, and consequently with a constant velocity. This velocity can be increased or diminished by lowering or raising the tube *d*; a position is therefore chosen for *d* so that the pressure in the calorimeter, which can be read off on the water-manometer, *n*, is about a centimetre less than that of the external air.

If the substance about to be burnt is a gas and enclosed in

C, an exit tube for D must then be chosen of suitable size to provide the necessary supply of gas per minute for the combustion. The tap *h* is next regulated until the gas in C shows an excess pressure of 2 to 3 cm. of mercury. Finally, the reservoir A of the oxygen apparatus is raised to the requisite height to provide a supply of oxygen corresponding to double the theoretical quantity necessary to support the flame of the burning gas.

Non-gaseous substances must be placed in the receptacle of the universal burner, where they are volatilized by means of the heat generated by the electric current passing through the spiral of the burner. The wires of the spiral, represented by *c* in the diagram, are connected with a regulator so that the intensity of the current can be controlled. Usually two Bunsen cells are required for a substance of high boiling-point; three of these cells are, however, sometimes necessary, whilst one cell may suffice for a very volatile body. Generally speaking, the vaporization is effected by means of a current of air mixed with oxygen. A mercury gasometer is used, or preferably an arrangement similar to that employed for the oxygen; but in any case the current of air is led into the burner through *b*. The electric and gas currents are then regulated until there is a clear flame of the requisite size. When the oxygen apparatus has been regulated in this manner all is ready for the combustion, which can be repeated under the same conditions without further adjustment.

As soon as the amount of water in the calorimeter has been weighed, the calorimeter prepared, the stirrer and thermometers put in their places, and communication with the absorption apparatus established, the motor is started, in order to obtain a uniform temperature in the water. The lower opening of the calorimeter, into which the burner fits, is then closed by means of an indiarubber cork, and the taps *a* and *b* of the aspirator are opened; in this manner a reduction of pressure (20 to 30 cm. of water) is produced in the system, when the taps are again closed; if the pressure indicated by the manometer *n* does not vary, it is a proof that all the joints are air-tight.

When working with a non-gaseous body, the electric current is first started in order to heat up the burner; one or two minutes afterwards the current of air is led into the volatilizer, where a flame of the size previously arranged for is produced.

One minute after these preparations are completed the calorimetric measurement is commenced, the time being noted on a stop-watch; the temperature of the air and also of the calorimeter is noted, and readings are again taken at the end of the second and third minutes, so that three observations for calculating the temperature of the calorimeter have been made before the end of the fourth minute, which is the moment when the combustion in the calorimeter should commence. Care must be taken to tap the thermometer before each reading, otherwise the observation may not be quite accurate.

During these four minutes the combustion proceeds with the required intensity; the contents of the gasholders B and C are noted, and at the end of the fourth minute the tap *a* of the aspirator is opened and the universal burner is placed in the opening of the calorimeter, which it closes tightly. The manometer *n*, which registers the pressure in the calorimeter, is then noted, and the tube *d* of the aspirator is raised or lowered until a depression of 1 cm. of water is registered.

All is then in order, and remains unchanged throughout the course of the combustion; this applies to the rate of flow of the oxygen and of the gas in the holder C, as well as to the vaporization brought about by the electric current in the burner, and to the regular working of the aspirator.

The conditions under which the combustion is proceeding is ascertained by watching the manometer, since any irregularity is at once detected by a considerable alteration in the level of the water. As long as the level remains unchanged the combustion is proceeding satisfactorily. Any variations of pressure which might arise during the course of the experiment, either from a regular rise of temperature in the calorimeter, or from a diminution in the resistance of the absorption apparatus, can be controlled by a small movement of the tube *d* of the aspirator. An increase of temperature in the calorimeter is always found to be proportional to the time.

When the temperature in the calorimeter has risen as high as is required, the combustion is interrupted by shutting the tap *d* of the gasholder C; the burner is then removed from the calorimeter and replaced by an indiarubber cork, through which a glass tube is inserted. This tube is connected up with the absorption tubes *9* and *10*, the first of which contains solid potash, the second a 40 per cent. solution of the alkali. The aspirator working continuously draws through the calorimeter a current of dry air freed from carbon dioxide in the tubes *9* and *10*. The rate of flow is regulated by means of the tube *d*, so that about 160 c.c. of gas pass in a minute; the apparatus is then left untouched for fifteen minutes, during which time the temperature is read every three minutes. The current of gas is noted by means of scales affixed to B and C; but only an approximate measure of this is required.

After the expiration of fifteen minutes the experiment is finished; the different parts of the apparatus are disconnected, and the absorption tubes *6*, *7*, and *8* are weighed.

9. Experimental Methods used in the Combustion of Compounds containing the Halogens, Sulphur, or Nitrogen.

Chlorine compounds.—The majority of the chlorine compounds of alcohol radicals, as well as the chlorine substitution products of the hydrocarbons, burn without difficulty in oxygen when they have a greater number of hydrogen than of chlorine atoms in the molecule, but other compounds can also be burnt in oxygen if some hydrogen be likewise added.

In order to bring about the combustion of these substances they are heated in the universal burner and vaporized by means of a current of hydrogen at a suitable temperature, so regulated that the flame burns without smoke or the deposition of graphite in the orifice of the tube. In each experiment the volume of gas is always the same, and the quantity of heat imparted to the calorimeter by the combustion can be determined with sufficient accuracy.

Amongst the chlorine compounds which can be burnt directly are three substances gaseous at ordinary temperatures,

i.e. the chlorides of methyl, ethyl, and vinyl; these are therefore collected in the mercury gasometer and burnt in the state of gas. Methyl chloride can be burnt alone, but the other two gases require to be first diluted, since their direct combustion leads to the deposition of graphite. To dilute these gases I make use of a mixture of oxygen and nitrogen, containing from 40 to 50 per cent. of the former; the chloride is then diluted in the gasometer with an equal volume of the mixed gases, and under these conditions the combustion takes place without further difficulty.

The other compounds, which are liquid at about 18° (with the exception of monochloropropylene, which boils at about 23° and mixes readily with oxygen so that it can be burnt in the state of gas), are heated in the universal burner and vaporized by means of a current of air containing from 40 to 50 per cent. of oxygen. Once the velocity of the gas current and the intensity of the electric current have been adjusted, it is easy to find the necessary relation between the current of vapour and of air in order to ensure a steady combustion. In these experiments, as in those already described, the amount of oxygen supplied is regulated by the condition that half of it should issue from the calorimeter with the products of the combustion.

In a normal combustion the products consist of carbon dioxide, water, and hydrogen chloride. The combustion chamber contains 10 grams of water, so that a solution of hydrochloric acid is formed therein. The whole of the chlorine, however, is never completely converted into hydrogen chloride, especially when the substance is poor in hydrogen; a part of it is therefore liberated as free chlorine, since oxygen decomposes gaseous hydrogen chloride the more readily the smaller the proportion of aqueous vapour present. The quantity of chlorine liberated is thus relatively greater for methyl chloride than for its higher homologues. On combustion of methyl chloride 6·5 per cent. of the total chlorine is liberated in the free state, whilst with ethyl chloride there is 2·4 per cent. of free chlorine, and with isobutyl chloride only 0·2 per cent.; ethylene chloride liberates 6 per cent. of its total chlorine in the free state, whilst ethylidene chloride yields only 4 per cent.

Thus, together with the carbon dioxide issuing from the calorimeter, there is not only a little chlorine, but also a small quantity of gaseous hydrogen chloride which escapes absorption in the water of the calorimeter.

In order, therefore, to be able to calculate the amount of heat in a normal combustion, it is necessary to determine the quantity of chlorine liberated in each of these three forms. For this purpose the gases issuing from the calorimeter are led into a tube containing several layers of pulverized and slightly moistened potassium iodide, separated by purified cotton-wool, where the free chlorine and part of the gaseous hydrogen chloride is absorbed. The gases then pass into a Liebig's bulb tube filled with a 10 per cent. solution of potassium iodide, to which 0·00005 gram-molecule of sodium thiosulphate is added for each experiment. Since the main object of this solution is to retain any iodine vapour carried over by the gas current, as well as small quantities of hydrogen chloride, the addition of thiosulphate provides a method of controlling the completeness of the absorption, and, generally speaking, the solution remains colourless. The current next passes into the apparatus already described for the absorption of the dry carbon dioxide, and finally reaches the aspirator.

As soon as the experiment is over, the solution of hydrochloric acid is poured out of the combustion chamber, which latter, together with the spiral tube, is rinsed out several times with water. The liquid thus obtained contains the whole of the hydrochloric acid absorbed in the calorimeter, and also a trace of dissolved chlorine, which can be determined by means of a few drops of a solution of potassium iodide and sodium thiosulphate; the amount of free chlorine is about 0·0004 gram-atom in such experiment. After this, litmus is added and the liquid titrated with soda. The amount of hydrochloric acid thus found, expressed in gram-molecules, is represented by ρ_0; this is, of course, equivalent to ρ_0 gram-atoms of chlorine.

The absorption tubes containing potassium iodide are then emptied out, the tubes rinsed, and the free iodine titrated with sodium thiosulphate. The amount found, expressed in gram-atoms, is equivalent to the amount of free chlorine; this is

represented by ρ, and must be added on to that found in the calorimeter.

After titrating the iodine with thiosulphate, litmus is added and the free acid is titrated. This value gives us the amount of gaseous hydrogen chloride issuing from the calorimeter, and which we shall represent in gram-atoms by ρ_1.

The three values, ρ_0, ρ, and ρ_1, thus found are of use in calculating the normal heat of combustion, in which hydrogen chloride and carbon dioxide are evolved in the gaseous state, and water as a liquid. They also afford a convenient means of ascertaining the purity of the substances investigated, since the sum $(\rho_0 + \rho + \rho_1)$, expressed in gram-atoms, gives us the total quantity of chlorine in the compound burnt, and this should correspond to the quantity of carbon dioxide determined, which is represented by a. There is a simple relation between these two values, since the combustion of $C_aH_bCl_c$ gives rise to $a + 44$ grams of carbon dioxide for each gram-atom of carbon; and we finally have the relation

$$a : c = \frac{a}{44} : (\rho_0 + \rho + \rho_1)$$

when the substance under examination is pure.

Thus the method employed for measuring the heat of combustion furnishes at the same time a quantitative determination of the amount of carbon and chlorine in the substance used. The value of this check on the purity of the substances investigated is clearly demonstrated by the experimental data given in the tables. Thus in two experiments with propyl chloride 4·8911 grams of carbon dioxide are formed, whilst the determination of the amount of chlorine was made as follows:—

Within the calorimeter as $HCl\rho_0$ . .	0·03573	gram-atom.	
Outside „ „ „ $HCl\rho$ . .	0·00032	„	„
„ „ „ „ $Cl\rho_1$ . . .	0·00093	„	„

or a total of 0·03698 gram-atom of chlorine.

As propyl chloride, C_3H_7Cl, contains three atoms of carbon for each atom of chlorine, the theoretical quantity of chlorine

to correspond to the amount of carbon dioxide found above should be

$$\frac{4{\cdot}8911}{3 \times 44} = 0{\cdot}03705 \text{ gram-atom of chlorine,}$$

which differs by 0·2 per cent. from that found directly.

With isobutyl chloride there were formed in two experiments 5·2665 grams of carbon dioxide, which is equivalent to

$$\frac{5{\cdot}2665}{4 \times 44} = 0{\cdot}02992 \text{ gram-atom of chlorine;}$$

and we find experimentally

ρ_0	0·02898
ρ	0·00025
ρ_1	0·00071
$\Sigma\rho$	0·02994 gram-atom of chlorine,

which is in agreement with the value calculated for the pure substance, and also with the complete combustion.

Experience has shown how difficult it is to obtain pure specimens of the chlorides of methyl and ethyl, these substances being always mixed with more or less of the corresponding ether.

The purest methyl chloride obtainable from Kahlbaum contains 0·0998 gram-molecule of dimethyl ether, CH_3OCH_3, for each gram-molecule of CH_3Cl. Another specimen prepared in my own laboratory by the interaction of zinc chloride, hydrochloric acid, and alcohol, and purified by means of concentrated sulphuric acid, contained 0·0203 gram-molecule of CH_3OCH_3 to 1 gram-molecule of CH_3Cl. Even in the action of phosphorus pentachloride upon alcohol some ether is formed, although in very small quantity; 1 gram-molcule of ethyl chloride prepared in this manner contains 0·008 gram-molecule of $(C_2H_5)_2O$. It is evident that in calculating the results of a combustion with such substances the influence of the possible impurities must be taken into account. This influence is, however, but small, and in practice presents few difficulties.

As in the experiments for determining the heats of combustion of halogen compounds two Liebig's absorption bulbs are used, one for the chlorine and the other for the carbon dioxide, care must be taken to avoid any variation of pressure in the combustion chamber. This result is attained as before by inserting two plugs of cotton-wool in the tube leading from the calorimeter to the first absorption tube. In all experiments with chlorine compounds indiarubber corks must as far as possible be avoided.

Bromine compounds.—The bromides studied, chiefly those of methyl, ethyl, propyl, and allyl, were burnt directly in oxygen. Methyl bromide is a gas at ordinary temperatures, so that it can be introduced into the burner and burnt like other gaseous substances. The other three bromides were vaporized by a currrent of air and heated in the universal burner. As all the bromides, especially those of propyl and allyl, have a tendency to deposit graphite in the orifice of the burner, it is best to use a mixture of equal volumes of oxygen and nitrogen for the combustion, and the heating is regulated so as to employ as large a quantity as possible of air for the vaporization.

The greater part of the bromine is liberated in the free state, some of this is absorbed by the water in the combustion chamber, while the rest is carried on with the current of air which issues from the calorimeter. Only a small fraction, varying from 10 to 25 per cent. according to the substance, of the bromine goes to form hydrobromic acid, and this is so completely absorbed by the water in the combustion chamber and spiral that scarcely a trace of it is found in the issuing gases. The combustion chamber usually contains 10 grams of water.

At the end of each experiment the contents of the combustion chamber and spiral are analyzed; the dissolved bromine is titrated by means of potassium iodide and thiosulphate, and the hydrobromic acid with a soda solution. As before, these quantities are expressed in gram-atoms, and are represented by ρ_2 and ρ_0. The gases issuing from the calorimeter are deprived of bromine by means of potassium iodide, in the manner described for the compounds of chlorine; the

quantity is determined by titrating with thiosulphate, and is expressed in gram-atoms by ρ. We then have

ρ_2 bromine in solution,
ρ_0 bromine as a solution of hydrobromic acid, } within the calorimeter.

ρ bromine in the state of vapour,
ρ_1 bromine as hydrobromic acid, } in the absorption tubes.

The sum of which represents the total bromine expressed as gram-atoms.

As the greater part of the bromine is evolved in the gaseous state, and carried out of the calorimeter with the other products of the combustion, the heat of combustion must naturally be calculated by assuming all of the hydrogen to go to form water, and the bromine, on the contrary, to be liberated as a gas. That is to say, for the substance $C_aH_bBr_c$ we have

a gram-molecules of carbon dioxide;
$0{\cdot}5\ b$ „ „ liquid water;
$0{\cdot}5\ c$ „ „ bromine vapour;

at atmospheric temperature. The following values were obtained in some of my earlier experiments :—

(H, Br)	8,440 calories
$(H, Br\ gas)$	12,260 „
$(H\,Br, Aq)$	19,940 „
(Br, Aq)	540 „
$(H, Br\ gas, Aq)$	32,200 „
$(Br\ gas, Aq)$	4,360 „

Each gram-atom of hydrogen which unites with bromine to form hydrobromic acid, and dissolves as such in the water of the calorimeter, thus liberates an amount of heat greater by 32,200 than if the bromine was evolved as a gas in the calorimeter; on the other hand, the gram-atom of hydrogen could unite with oxygen to give rise to a half gram-molecule of water, and in doing this would liberate 34,180 calories, if it had not combined with the bromine. The formation of the solution of hydrobromic acid therefore diminishes the theoretical quantity

of heat by 1980 calories for each gram-atom of bromine involved, or the quantity of heat found experimentally by $\rho_0 1980$ calories. On the other hand, this value will be increased by ρ_2 3460 calories by the solution of ρ_2 gram-atoms of bromine vapour in the water of the combustion chamber. The amount of hydrobromic acid which can be detected in the products of combustion outside the calorimeter, or ρ_1, is so small that its influence on the result is negligible. Neither is there any need to take into consideration the different degrees of dilution which may occur in the calorimeter, since the dilution is always so great (100 molecules of water to 1 molecule of hydrobromic acid) that the heat of absorption will vary only by a few units. To find the true heat of combustion in the reaction described above, it is necessary to increase the value found experimentally by

$$\rho_0 \text{ 1890 cal.} - \rho_2 \text{ 4360 cal.}$$

As the water equivalent of the calorimeter and its contents in the experiments with the bromides is 2957·4 grams, it is simpler, in calculating the experimental results, to divide the correction given above by this number, and to raise the observed temperature of the calorimeter by the corresponding amount.

Iodine compounds.—The iodine compounds of alcohol radicals burn easily in oxygen when heated in the universal burner and vaporized by means of a current of air. In atmospheric air the flame of methyl iodide is extinguished immediately after being kindled, but by mixing it with oxygen in the burner a flame can be obtained without using the calorimeter. The two iodides studied (CH_3I and C_2H_5I), even when burnt in oxygen, give rise to feebly luminous flames.

On combustion in oxygen the products are carbon dioxide, water, and iodine. No hydriodic acid is formed, since after dissolving the iodine deposited in the potassium iodide solution, and decolorizing it by means of sodium thiosulphate, we are left with a neutral solution.

The iodine is all deposited in crystals upon the cold surface of the platinum walls of the combustion chamber; only a very

small fraction, corresponding to the tension of iodine vapour at the temperature of the calorimeter (18° to 20°), is carried along with the current of gas. The gases issuing from the calorimeter pass through a Liebig's absorption bulb containing water in which 0·0004 gram-molecule of sodium thiosulphate is dissolved. This solution still remained colourless after two combustions had been performed, so that the quantity of iodine carried over did not amount to 0·0004 gram-atom, while in two experiments carried out upon methyl iodide 0·0777 gram-atom, or 9·87 grams of iodine were deposited in the combustion chamber.

The result of the combustion is to liberate the whole of the iodine in the solid state, and in order to find the corresponding values, assuming the iodine to be present as vapour at 18°, it is necessary to know the amount of heat required to convert solid iodine at 18° into vapour at the same temperature and under normal pressure. To do this we make use of the following data, namely, the heat of vaporization of iodine at the boiling-point, 23·97 cal.; the specific heat of liquid iodine, 0·108 cal.; and the heat of fusion, 11·71 cal. (Favre and Silbermann, *Annales de chimie et de physique*, [3] xxxvii. 469); also Regnault's value of 0·0541 cal. for the specific heat of solid iodine; and the value of 0·0349 cal. given by K. Strecker for the specific heat of iodine vapour (Wiedermann's *Annalen*, xiii. 40). If we take the boiling-point of iodine as 180°, and the melting-point as 107°, we can calculate the quantity of heat required to vaporize 1 gram of solid iodine as follows:—

$$(107-18)0{\cdot}0541 + 11{\cdot}71 + (180-107)0{\cdot}1082 + 23{\cdot}95 = 48{\cdot}37 \text{ cal.}$$

To cool the vapour from 180° to 18° without deposition of solid or liquid iodine would give

$$(180 - 18)0{\cdot}0349 = 5{\cdot}65 \text{ calories.}$$

Thus the total quantity of heat absorbed by 1 gram of iodine will be equal to 42·72 cal., or 5426 cal. per gram-atom. Consequently the heat of combustion will be 5426 cal. less if we assume the iodine to be present as gas instead of as solid.

Sulphur compounds.—These substances were burnt in oxygen in the calorimeter in the same way as other volatile organic compounds. Non-gaseous compounds were vaporized in the universal burner in the usual manner by means of a current of air containing 50 per cent. of oxygen. The products of combustion are carbon dioxide, water, sulphur dioxide, and sulphur trioxide.

The water (10 grams) in the combustion chamber retains the greater part of the sulphur trioxide and a smaller fraction of the dioxide, while the remainder passes on with the other gaseous products into the absorption tubes. At first the gases pass through a small flask containing solid iodine partially dissolved in a solution of potassium iodide; the quantity of iodine used depends upon the proportion of sulphur in the compound. In the experiments with carbon disulphide it was necessary to use from 11 to 12 grams of iodine, and the volume of the 10 per cent. potassium iodide solution was about 30 c.c. After the current of gas has been freed from sulphur dioxide by the iodine solution it still contains the greater part of the trioxide, either in the form of gas or as dense vapours of sulphuric acid, and flows on through a Liebig's bulb tube which acts as a control. In order to remove completely this cloud of sulphuric acid, the current is led through a layer, 2 cm. thick, of powdered calcium chloride placed in an enlarged part of the tube through which the gas flows. The gases then pass on to the drying tubes, and finally reach the absorption apparatus, where the carbon dioxide is removed as in the other experiments described.

Thus, after the combustion, part of the sulphur is found as sulphuric and as sulphurous acid in the combustion chamber; the remainder issues from the calorimeter in the form of sulphur dioxide gas and as the vapour of sulphur trioxide, and is absorbed by the iodine solution and converted into sulphuric acid. The amount of each of these four products must be determined as follows: After the combustion is finished, the contents of the combustion chamber and of the platinum spiral are washed out, and the sulphurous acid is titrated by means of an iodine solution of known strength;

the amount, expressed in gram-molecules, is represented by s_1; the solution is then titrated with soda (in all my titrations the quantity of liquid is determined by weight and not by volume). Let b represent the amount of acid in gram-molecules. Then, since for each molecule of sulphurous acid which is oxidized to sulphuric acid two molecules of hydriodic acid are formed, the amount of sulphuric acid which was present before oxidation was

$$s_2 = b - 2s_1.$$

The acid absorbed outside the calorimeter is also determined; the absorption tubes are emptied and rinsed out, and the free iodine titrated with thiosulphate. The value thus found, deducted from the weight of iodine taken, gives the amount used up in oxidizing the sulphurous acid formed. If we represent this difference, expressed in gram-molecules of iodine, by s_3, this gives the amount of sulphurous acid formed, also expressed in gram-molecules. The total acid is then determined by titration with soda; and if the quantity of soda solution required for neutralization, expressed in gram-equivalents, be represented by d, the amount of sulphuric anhydride originally present will be

$$s_4 = d - 2s_3.$$

The products of combustion are therefore made up as follows:—

s_1 gram-molecules	SO_2	in aqueous solution within
s_2 „ „	SO_3	the calorimeter.
s_3 „ „	SO_2	in the absorption tubes out-
s_4 „ „	SO_3	side the calorimeter.

From the sum of these values the total amount of sulphur expressed in gram-atoms can be calculated. If now we suppose that the compound under examination contains a gram-atoms of carbon for each gram-atom of sulphur, and if α grams of carbon dioxide are formed in the combustion, we can establish the following relation for the combustion of the pure substance:—

$$\frac{\alpha}{44 \cdot a} = s_1 + s_2 + s_3 + s^4,$$

so that the determination of the amount of sulphur and of carbon in the products of the combustion furnishes a means of ascertaining the purity of the substance used.

As the heat of combustion is calculated on the assumption that the products are carbon dioxide, water, nitrogen, and gaseous oxides of sulphur, the experimental value requires certain corrections. The heat of absorption of sulphur dioxide is 7700 calories per gram-molecule. The heat of oxidation of the gaseous oxides of sulphur, and the solution in water of the sulphuric acid formed ($\dot{S}O_2$, O, Aq) is 71,330 calories when the amount of water present is very large; but in the actual experiment the value is only 69,000 calories, owing to the smaller amount of water. The sulphuric acid vapour may be regarded as the hydrate of sulphur trioxide, and the thermal effect of its formation starting from gaseous sulphur dioxide is 53,430 calories. The observed heat of combustion is thus

$$7700 \text{ cal. } s_1 + 69{,}000 \text{ cal. } s_2 + 53{,}430 \text{ cal. } s_4 = \text{P}$$

greater than the theoretical value.

Nitrogen compounds.—Cyanogen and hydrocyanic acid are collected over mercury in the gasometer and burnt as gases in the usual way; hydrocyanic acid can easily be vaporized at ordinary temperatures by means of a small quantity of nitrogen.

The combustion of esters, such as ethyl nitrate, takes place with production of nitric acid; 1 gram-molecule of the ester gives rise to 0·047 gram-molecule of N_2O_5Aq. I have already shown that the formation of an aqueous solution of N_2O_5, starting from nitrogen, oxygen, and water, gives rise to 29,820 calories, so that the experimental result must be reduced by $0{\cdot}047 \times 29{,}820$, or 14,000, calories in order to find the heat of a normal combustion where no nitric acid is formed.

The combustion of nitromethane, similarly to that of the other members of this group, was carried out in the usual manner by vaporizing the substance at a suitable temperature in the universal burner. A small amount of nitric acid is always formed, which condenses in the combustion chamber, as well as some nitric peroxide which is carried along with

the other products of combustion into the absorption apparatus, where it is retained in the tubes filled with chromic and sulphuric acids. The observed heat of combustion must be corrected so as to allow for the formation of these oxides of nitrogen. As has been stated above, the heat of formation of 1 gram-molecule of N_2O_5Aq is 29,820 calories, and this value must be deducted for each gram-molecule of nitrogen which combines with oxygen and water to form nitric acid. On the other hand, we may neglect the thermal effect due to the formation of nitric peroxide, since it amounts only to -4000 calories per gram-molecule of nitrogen.

An examination of the thermal properties of inorganic substances presents fewer practical difficulties than is the case when dealing with organic compounds, so that it has not been considered necessary to give a detailed description of any such experiments. Diagrams of the apparatus used have, however, been reproduced, and it is hoped that these will suffice to give a general idea of the methods employed.

PART I

FORMATION AND PROPERTIES OF AQUEOUS SOLUTIONS

CHAPTER I

ABSORPTION OF GASES AND SOLUTION OF LIQUIDS AND SOLIDS IN WATER

A. Numerical Results.

When a substance is dissolved in water a thermal effect is observed, which may be positive or negative according to the nature of the substance. The heat of solution is not a constant magnitude for the same substance, but is determined by the amount of water contained in the solution, as well as by the temperature of the water. This dependence of the heat of solution upon the quantity and temperature of the water will form the subject-matter of Part I., and the numbers quoted in the following tables, therefore, hold good only at a temperature of about 18° C., and for the particular amount of water specified in the tables for each individual substance. All magnitudes are calculated for the gram-molecule of the dissolved substance, for example, Na_2SO_4 and NaCl; and the amount of water used is, as a rule, 400 and 200 gram-molecules respectively, according to the valency of the substance, so that the concentrations of the resulting solutions agree with those usually employed in thermochemical reactions in aqueous solution.

The tables include the heats of solution of all the substances that I have investigated; the *first* subdivision gives the heats of solution of the most frequently occurring gases, the *second* and *third* the heats of solution, at about 18° C., of liquid and solid compounds between non-metals, and in the *fourth*

subdivision are recorded my very numerous determinations of the heats of solution of the oxides, hydroxides, halides, and oxy-salts of the metals.

Naturally many of these substances do not form real aqueous solutions, since the compounds are decomposed by water, and the thermal effect observed in such cases corresponds to the decomposition taking place; this applies, for example, to carbonyl chloride, carbonyl sulphide, and the chlorides of phosphorus, arsenic, etc.; only very few substances, as, for instance, the chlorides of silicon, titanium, antimony, bismuth, and tellurium, are not completely dissolved by water.

Most of the substances investigated were readily soluble in water, and their heats of solution could therefore easily be measured by direct experiment; but for some sparingly soluble substances special methods had to be adopted.

The amount of water in hydrated salts was estimated by analysis, and the result of this is given in the table for each particular salt. In drying hydrated salts which crystallize from solutions, care must be taken that the number of molecules of water remaining in the salt is not below the normal, and the drying must, therefore, be discontinued as soon as analysis shows that the amount of water in the molecule is only a very little greater than that required for the normal salt; a trace of moisture will not affect the heat of solution to any appreciable extent, while a considerable influence is exerted when the number of water molecules falls below the normal value. The determination of the heat of solution of a hydrated salt can even be used with advantage to determine accurately the normal amount of water, a method which I have employed for ascertaining the molecular formulæ of some hydrated salts; for example, $BaI_2 . 7H_2O$ and $HAuCl_4 . 4H_2O$.

For the atomic weights of the non-metals O is taken as 16 and H_2 as 2·01.

Cl	35·45	C	12·00	Bi	208·00
Br	80·00	P	31·00	S	32·00
I	126·90	As	75·00	Se	79·00
N	14·00	Sb	120·00	Te	127·60

The atomic weights employed for the metals will be found in the tables containing the respective compounds.

TABLE I.

Heats of Absorption and of Solution.

(*a*) *Non-metals and their Compounds.*

1. Gases.

Substance (gaseous).	Molecular formula.	Amount of water in the solution.	Heat of absorption of 1 gram-molecule of the substance.
Hydrogen chloride . .	HCl	300 mol.	17,315 c
Hydrogen bromide . .	HBr	400 ,,	19,940
Hydrogen iodide . .	HI	500 ,,	19,210
Water vapour at 18° .	H_2O	—	10,430
Hydrogen sulphide . .	H_2S	900 ,,	4,560
Ammonia	NH_3	200 ,,	8,430
Chlorine monoxide . .	Cl_2O	800 ,,	9,440
Sulphur dioxide . . .	SO_2	250 ,,	7,700
Carbon dioxide . . .	CO_2	1500 ,,	5,880
Chlorine	Cl_2	—	4,870
Bromine gas at 17° . .	Br_2 gas	—	7,640
Carbonyl chloride . .	$COCl_2$	—	57,970[1]
Carbonyl sulphide . .	COS	—	4,740[2]
Nitric peroxide . .	NO_2	300 ,,	13,875[3]
Nitrogen tetroxide . .	N_2O_4	600 ,,	14,150[4]

[1] $COCl_2$ is completely decomposed in solution to CO_2Aq and 2HClAq.
[2] COS ,, ,, ,, ,, CO_2Aq and H_2SAq.
[3] Valid for the completely dissociated molecule.
[4] Valid for the non-dissociated molecule.

2. Liquids.

Substance (liquid).	Molecular formula.	Amount of water in the solution.	Heat of solution of 1 gram-molecule of the substance.
Bromine	Br_2	600 mol.	1,080 c
Sulphur dioxide (liquid)	SO_2	300 ,,	1,500
Sulphur trioxide (liq.)	SO_3	1600 ,,	39,170
Pyrosulphuric acid (liq.)	$H_2S_2O_7$	1600 ,,	54,320
Sulphuric acid (liq.) .	H_2SO_4	1600 ,,	17,850
Sulphuric acid, hydrate (liq.)	$H_2SO_4 . H_2O$	1600 ,,	11,470
Sulphuryl chloride . .	SO_2Cl_2	800 ,,	62,900
Nitric acid	HNO_3	300 ,,	7,480
Phosphoric acid (liq.) .	H_3PO_4	200 ,,	5,350
Phosphorous acid (liq.)	H_3PO_3	120 ,,	2,940
Hypophosphorous acid (liq.)	H_3PO_2	200 ,,	2,140
Phosphorus trichloride .	PCl_3	1000 ,,	65,140
Phosphorus oxychloride	$POCl_3$	1100 ,,	72,190
Arsenic trichloride . .	$AsCl_3$	900 ,,	17,580
Antimony pentachloride	$SbCl_5$	1100 ,,	35,200
Silicon tetrachloride .	$SiCl_4$	3000 ,,	69,260
Titanic chloride . . .	$TiCl_4$	1600 ,,	57,870
Stannic chloride . . .	$SnCl_4$	300 ,,	29,920
Formic acid	CH_2O_2	200 ,,	150
Acetic acid	$C_2H_4O_2$	200 ,,	375

3. Solids.

Substance (solid).	Molecular formula.	Amount of water in the solution.	Heat of solution of 1 gram-molecule of the substance.
Iodine pentoxide . .	I_2O_5	—	− 1,790 c
Iodic acid	HIO_3	200 mol.	− 2,170
Periodic acid	H_5IO_6	550 ,,	− 1,380
Phosphoric acid (solid) .	H_3PO_4	120 ,,	+ 2,690
Phosphorous acid (solid)	H_3PO_3	120 ,,	− 130
Hypophosphorous acid (solid)	H_3PO_2	200 ,,	− 170
Phosphorus pentoxide .	P_2O_5	550 ,,	+ 35,600
Arsenic pentoxide . .	As_2O_5	—	+ 6,000
Arsenic acid	H_3AsO_4	230 ,,	− 400
Arsenious acid . . .	As_2O_3	—	− 7,550
Selenium dioxide . .	SeO_2	200 ,,	− 920
Boracic acid (cryst.) .	$B_2O_3 . 3H_2O$	800 ,,	− 10,790
Phosphorus pentachloride	PCl_5	1800 ,,	+12,3440

Substance (solid).	Molecular formula.	Amount of water in the solution.	Heat of solution of 1 gram-molecule of the substance.
Antimony trichloride .	$SbCl_3$	—	+ 8,910 c
Bismuth trichloride . .	$BiCl_3$	—	+ 7,830
Selenium tetrachloride .	$SeCl_4$	1600 mol.	+ 30,370
Tellurium tetrachloride	$TeCl_4$	1200 ,,	+ 20,340
Ammonium chloride .	NH_4Cl	200 ,,	− 3,880
Ammonium bromide .	NH_4Br	200 ,,	− 4,380
Ammonium iodide . .	NH_4I	200 ,,	− 3,550
Ammonium nitrate . .	NH_4NO_3	200 ,,	− 6,320
Ammonium sulphate .	$(NH_4)_2SO_4$	400 ,,	− 2,370
Ammonium hydrogen sulphate . . .	NH_4HSO_4	200 ,,	− 20
Hydroxylammonium chloride . . .	NH_3OHCl	200 ,,	− 3,650
Hydroxylammonium sulphate . . .	$(NH_3O)_2H_2SO_4$	660 ,,	− 960
Triethylsulphonium iodide	$S(C_2H_5)_3I$	267 ,,	− 5,750
Oxalic acid	$C_2H_2O_4$	300 ,,	− 2,260
Oxalic acid (cryst.) . .	$C_2H_2O_4 . 2H_2O$	530 ,,	− 8,590
Tartaric acid	$C_4H_6O_6$	400 ,,	− 3,600
Citric acid . . .	$C_6H_8O_7$	600 ,,	− 4,100
	$C_6H_8O_7 . H_2O$	400 ,,	− 6,430
Aconitic acid	$C_6H_6O_6$	300 ,,	− 4,180

(*b*) *Compounds of the Metals: Oxides, Hydroxides, and Salts.*

Metal.	Molecular formula.	Amount of water in the solution.	Heat of solution of 1 gram-molecule of the substance.	Amount of water according to analysis.
Potassium 39·15	KCl	200 mol.	− 4,440 c	
	KBr	200 ,,	− 5,080	
	KI	200 ,,	− 5,110	
	KCN	175 ,,	− 3,010	
	KOH	250 ,,	+13,290	
	KNO_3	200 ,,	− 8,520	
	$KClO_3$	400 ,,	−10,040	
	$KBrO_3$	200 ,,	− 9,760	
	KIO_3	500 ,,	− 6,780	
	K_2CO_3	400 ,,	+ 6,490	
	$K_2CO_3 . \frac{1}{2}H_2O$	400 ,,	+ 4,280	0·507
	$K_2CO_3 . \frac{3}{2}H_2O$	400 ,,	− 380	1·550
	K_2SO_4	400 ,,	− 6,380	
	$KHSO_4$	200 ,,	− 3,800	

Metal.	Molecular formula.	Amount of water in the solution.	Heat of solution of 1 gram-molecule of the substance.	Amount of water according to analysis.
Potassium 39·15	$K_2S_2O_6$	500 mol.	−13,010 c	
	$K_2S_3O_6$	500 ,,	−12,460	
	$K_2S_4O_6$	500 ,,	−13,150	
	$K_2Cr_2O_7$	400 ,,	−16,700	
	$K_2Mn_2O_8$	1000 ,,	−20,790	
	$K_2C_2O_4 . H_2O$	800 ,,	− 7,410	
	$KC_2H_3O_2$	200 ,,	+ 3,340	
Sodium 23·05	NaCl	100 ,,	− 1,180	
	NaBr	200 ,,	− 190	
	$NaBr . 2H_2O$	300 ,,	− 4,710	
	NaI	200 ,,	+ 1,220	
	$NaI . 2H_2O$	300 ,,	− 4,010	
	NaOH	200 ,,	+ 9,940	
	$NaNO_3$	200 ,,	− 5,030	
	Na_2CO_3	400 ,,	+ 5,640	
	$Na_2CO_3 . H_2O$	400 ,,	+ 2,250	
	$Na_2CO_3 . 2H_2O$	400 ,,	+ 20	
	$Na_2CO_3 . 10H_2O$	400 ,,	−16,160	
	Na_2SO_4	400 ,,	+ 460	fused
		400 ,,	+ 170	effloresced[1]
	$Na_2SO_4 . H_2O$	400 ,,	− 1,900	
	$Na_2SO_4 . 10H_2O$	400 ,,	−18,760	10·00
	$NaHSO_4$	200 ,,	+ 1,190	
	$Na_2S_2O_6$	400 ,,	− 5,370	0·09
	$Na_2S_2O_6 . 2H_2O$	400 ,,	−11,650	2·13
	$Na_2S_2O_3 . 5H_2O$	400 ,,	−11,370	
	Na_2HPO_4	400 ,,	+ 5,640	
	$Na_2HPO_4 . 2H_2O$	400 ,,	− 390	
	$Na_2HPO_4 . 12H_2O$	400 ,,	−22,830	12·09
	$Na_2NH_4PO_4 . 4H_2O$	800 ,,	−10,750	
	$Na_4P_2O_7$	800 ,,	+11,850	
	$Na_4P_2O_7 . 10H_2O$	800 ,,	−11,670	10·27
	$Na_2B_4O_7 . 10H_2O$	1600 ,,	−25,860	
	$NaC_2H_3O_2 . 3H_2O$	400 ,,	− 4,810	
	$NaC_2H_3O_2$	200 ,,	+ 3,870	
Lithium 7·0	LiCl	230 ,,	+ 8,440	
	$LiNO_3$	100 ,,	+ 300	
	Li_2SO_4	200 ,,	+ 6,050	
	$Li_2SO_4 . H_2O$	400 ,,	+ 3,410	1·10
Barium 137·2	$BaCl_2$	400 ,,	+ 2,070	
	$BaCl_2 . 2H_2O$	400 ,,	− 4,930	
	$BaBr_2$	400 ,,	+ 4,980	
	$BaBr_2 . 2H_2O$	400 ,,	− 4,130	2·00
	$BaI_2 . 7H_2O$	500 ,,	− 6,850	7·17

[1] *Note by Translator.*—The effloresced salt would be of uncertain composition, but would be sure to contain some water.

Metal.	Molecular formula.	Amount of water in the solution.	Heat of solution of 1 gram-molecule of the substance.	Amount of water according to analysis.
	BaO	—	+34,520 c	
	$Ba(OH)_2$	—	+12,260	
	$Ba(OH)_2 . 8H_2O$	400 mol.	−15,210	7·98
	$Ba(NO_3)_2$	400 ,,	− 9,400	
Barium	$Ba(ClO_3)_2 . H_2O$	600 ,,	−11,240	
137·2	$BaS_2O_6 . 2H_2O$	400 ,,	− 6,930	2·00
	$BaSO_4$	—	− 5,580	see V.
	$Ba(H_2PO_2)_2 . H_2O$	800 ,,	+ 290	
	$Ba(C_2H_5SO_4)_2 2H_2O$	800 ,,	− 4,970	
	$Ba(C_2H_3O_2)_2 . 3H_2O$	800 ,,	− 1,150	
	$SrCl_2$	400 ,,	+11,140	
	$SrCl_2 . 6H_2O$	400 ,,	− 7,500	6·00
	$SrBr_2$	400 ,,	+16,110	
	$SrBr_2 . 6H_2O$	400 ,,	− 7,220	6·18
Strontium	SrO	—	+29,340	
87·5	$Sr(OH)_2$	—	+11,640	
	$Sr(OH)_2 . 8H_2O$	—	−14,640	7·95
	$Sr(NO_3)_2$	400 ,,	− 4,620	
	$Sr(NO_3)_2 . 4H_2O$	400 ,,	−12,300	4·02
	$SrS_2O_6 . 4H_2O$	400 ,,	− 9,250	4·16
	$CaCl_2$	300 ,,	+17,410	
	$CaCl_2 . 6H_2O$	400 ,,	− 4,310	6·07
	$CaBr_2$	400 ,,	+24,510	
	$CaBr_2 . 6H_2O$	400 ,,	− 1,090	6·07
	CaI_2	400 ,,	+27,690	
Calcium	CaO	2500 ,,	+18,330	
40·0	$Ca(OH)_2$	2500 ,,	+ 2,790	
	$Ca(NO_3)_2$	400 ,,	+ 3,950	
	$Ca(NO_3)_2 . 4H_2O$	400 ,,	− 7,250	4·20
	$CaS_2O_6 . 4H_2O$	400 ,,	− 7,970	4·14
	$CaSO_4$	—	+ 4,440	
	$CaSO_4 . 2H_2O$	—	− 300	
	$MgCl_2$	800 ,,	+35,920	
	$MgCl_2 . 6H_2O$	400 ,,	+ 2,950	6·11
	$Mg(OH)_2$	—	0	
	$Mg(NO_3)_2 . 6H_2O$	400 ,,	− 4,220	6·06
Magnesium	$MgS_2O_6 . 6H_2O$	400 ,,	− 2,960	6·22
24·0	$MgSO_4$	400 ,,	+20,280	
	$MgSO_4 . H_2O$	400 ,,	+13,300	
	$MgSO_4 . 7H_2O$	400 ,,	− 3,800	
	$K_2Mg(SO_4)_2 . 6H_2O$	600 ,,	−10,020	6·20
	$K_2Mg(SO_4)_2$	600 ,,	+10,600	
Aluminium	Al_2Cl_6	2500 ,,	+153,690	
27·4	$K_2Al_2(SO_4)_4 . 24H_2O$	2400 ,,	− 20,240	
Cerium	$Ce_2(SO_4)_3 . 4 \cdot 4H_2O$	1200 ,,	+ 16,130	4·38
Yttrium	$Y_2(SO_4)_3 . 8H_2O$	1200 ,,	+ 10,680	8·04
Didymium	$Di_2(SO_4)_3 . 8H_2O$	1200 ,,	+ 6,320	8·82
Lanthanum	$La_2(SO_4)_3 . 8H_2O$	—	+ 4,000 ?	8·9

Metal.	Molecular formula.	Amount of water in the solution.	Heat of solution of 1 gram-molecule of the substance.	Amount of water according to analysis.
Beryllium	$BeSO_4 . 4H_2O$	400 mol.	+ 1,100 c	4·00
Erbium	$Er_2(C_2H_3O_2)_6 . 8H_2O$	3000 ,,	+ 1,360	
Chromium	$K_2Cr_2(SO_4)_4 . 24H_2O$	1600 ,,	− 19,130	
52	$K_2Cr_2O_7$	400 ,,	− 16,700	
	$ZnCl_2$	300 ,,	+ 15,630	
	$ZnBr_2$	400 ,,	+ 15,030	
	ZnI_2	400 ,,	+ 11,310	
	$Zn(NO_3)_2 . 6H_2O$	400 ,,	− 5,840	5·94
Zinc	$ZnS_2O_6 . 6H_2O$	400 ,,	− 2,420	6·08
65·0	$ZnSO_4$	400 ,,	+ 18,430	
	$ZnSO_4 . H_2O$	400 ,,	+ 9,950	
	$ZnSO_4 . 7H_2O$	400 ,,	− 4,260	7·00
	$K_2Zn(SO_4)_2$	600 ,,	+ 7,910	
	$K_2Zn(SO_4)_2 . 6H_2O$	600 ,,	− 11,900	6·05
	$CdCl_2$	400 ,,	+ 3,010	
	$CdCl_2 . H_2O$	400 ,,	+ 760	
	$CdCl_2 . 2H_2O$	400 ,,	− 2,280	2·10
	$CdBr_2$	400 ,,	+ 440	
Cadmium	$CdBr_2 . 4H_2O$	600 ,,	− 7,290	4·06
112	CdI_2	400 ,,	− 960	
	$CdSO_4$	400 ,,	+ 10,740	
	$CdSO_4 . H_2O$	400 ,,	+ 6,050	
	$CdSO_4 . \frac{8}{3}H_2O$	400 ,,	+ 2,660	2·66
	$Cd(NO_3)_2 . H_2O$	400 ,,	+ 4,180	1·00
	$Cd(NO_3)_2 . 4H_2O$	400 ,,	− 5,040	4·19
	$MnCl_2$	350 ,,	+ 16,010	
	$MnCl_2 . 4H_2O$	400 ,,	+ 1,540	3·88
	$MnSO_4$	400 ,,	+ 13,790	
	$MnSO_4 . H_2O$	400 ,,	+ 7,820	
Manganese	$MnSO_4 . 5H_2O$	400 ,,	+ 40	5·02
55·0	$MnS_2O_6 . 6H_2O$	400 ,,	− 1,930	6·04
	$Mn(NO_3)_2 . 6H_2O$	400 ,,	− 6,150	
	$K_2Mn_2O_8$	1000 ,,	− 20,790	
	$K_2Mn(SO_4)_2$	600 ,,	+ 6,380	
	$K_2Mn(SO_4)_2 . 4H_2O$	600 ,,	− 6,435	4·15
	$FeCl_2$	350 ,,	+ 17,900	
Iron	$FeCl_2 . 4H_2O$	400 ,,	+ 2,750	
56·0	Fe_2Cl_6	2000 ,,	+ 63,360	
	$FeSO_4 . 7H_2O$	400 ,,	− 4,510	
	$CoCl_2$	400 ,,	+ 18,340	
Cobalt	$CoCl_2 . 6H_2O$	400 ,,	− 2,850	5·80
59	$CoSO_4 . 7H_2O$	800 ,,	− 3,570	7·10
	$Co(NO_3)_2 . 6H_2O$	400 ,,	− 4,960	6·08
	$NiCl_2$	400 ,,	+ 19,170	
Nickel	$NiCl_2 . 6H_2O$	400 ,,	− 1,160	6·02
58·5	$NiSO_4 . 7H_2O$	800 ,,	− 4,250	7·03
	$NiS_2O_6 . 6H_2O$	400 ,,	− 2,420	6·08
	$Ni(NO_3)_2 . 6H_2O$	400 ,,	− 7,470	5·93

Metal.	Molecular formula.	Amount of water in the solution.	Heat of solution of 1 gram-molecule of the substance.	Amount of water according to analysis.
Copper 63·5	$CuCl_2$	600 mol.	+ 11,080 c	
	$CuCl_2 . 2H_2O$	400 ,,	+ 4,210	
	$CuBr_2$	400 ,,	+ 8,250	
	$CuSO_4$	400 ,,	+ 15,800	
	$CuSO_4 . H_2O$	400 ,,	+ 9,340	
	$CuSO_4 . 5H_2O$	400 ,,	− 2,750	
	$K_2Cu(SO_4)_2$	600 ,,	+ 9,400	
	$K_2Cu(SO_4)_2 . 6H_2O$	600 ,,	− 13,570	6·17
	$CuS_2O_6 . 5H_2O$	400 ,,	− 4,870	5·00
	$Cu(NO_3)_2 . 6H_2O$	400 ,,	− 10,710	6·01
Thallium 204	Tl_2Cl_2	9000 ,,	− 20,200	
	Tl_2O	570 ,,	− 3,080	
	$Tl_2(OH)_2$	470 ,,	− 6,310	
	Tl_2SO_4	1600 ,,	− 8,280	
	$Tl_2(NO_3)_2$	600 ,,	− 19,940	
Lead 207	$PbCl_2$	1800 ,,	− 6,800	
	$PbBr_2$	2500 ,,	− 10,040	
	$Pb(NO_3)_2$	400 ,,	− 7,610	
	$PbS_2O_6 . 4H_2O$	400 ,,	− 8,540	4·14
	$Pb(C_2H_3O_2)_2 . 3H_2O$	800 ,,	− 6,140	
Tin 119	$SnCl_2$	300 ,,	+ 350	
	$SnCl_2 . 2H_2O$	200 ,,	− 5,370	
	$K_2SnCl_4 . H_2O$	600 ,,	− 13,420	
	$SnCl_4$	300 ,,	+ 29,920	
	K_2SnCl_6	800 ,,	− 3,380	
Mercury 200	$HgCl_2$	300 ,,	− 3,300	
	$K_2HgCl_4 . H_2O$	600 ,,	− 16,390	
	K_2HgBr_4	600 ,,	− 9,750	
	K_2HgI_4	800 ,,	− 9,810	
Silver 108	$Ag_2(NO_3)_2$	400 ,,	− 10,880	
	Ag_2SO_4	1400 ,,	− 4,480	
	$Ag_2S_2O_6 . 2H_2O$	400 ,,	− 10,360	2·38
Gold 196	$AuCl_3$	900 ,,	+ 4,450	2·10
	$AuCl_3 . 2H_2O$	600 ,,	− 1,690	4·10
	$HAuCl_4 . 4H_2O$	400 ,,	− 5,830	
	$AuBr_3$	2000 ,,	− 3,760	5·28
	$HAuBr_4 . 5H_2O$	1000 ,,	− 11,400	
Palladium 106	K_2PdCl_4	800 ,,	− 13,630	
	K_2PdCl_6	—	− 15,000?	
Platinum 198	K_2PtCl_4	600 ,,	− 12,220	
	$(NH_4)_2PtCl_4$	660 ,,	− 8,480	
	K_2PtCl_6	—	− 13,760	
	Na_2PtCl_6	800 ,,	+ 8,540	
	$Na_2PtCl_6 . 6H_2O$	900 ,,	− 10,630	5·98
	K_2PtBr_4	800 ,,	− 10,630	
	K_2PtBr_6	2000 ,,	− 12,260	
	Na_2PtBr_6	600 ,,	+ 9,990	
	$Na_2PtBr_6 . 6H_2O$	800 ,,	− 8,550	6·05
	$(NH_3)_4PtCl_2 . H_2O$	400 ,,	− 8,760	

B. Theoretical Results.

1. To draw conclusions of general application concerning the thermal effect due to the solution of substances in water is necessarily a difficult problem, owing to the variety of operations which in some cases come into play; but certain general conclusions can nevertheless be drawn from the large amount of material available.

The *first subdivision* treats of the heat of absorption of gaseous substances, which is naturally always *positive*, since the substance changes its state from gas to liquid, and the thermal effect will consequently correspond to the heat of vaporization, provided that no secondary reactions take place, which will almost always be the case.

The *second subdivision* gives the heats of solution of some few liquids; and here, too, it is noticed that the thermal effect is always *positive*, which again is easily explained. For even if no chemical action takes place between the water and the liquid dissolved therein (as, for instance, in the formation or decomposition of hydrates), there must still be some effect produced, since the molecules of the substance and of the water will form a homogeneous liquid wherein all the molecules have a uniform motion; but such an equalization of molecular velocities, with the retention of the acquired momentum, must result in a development of heat.

Thence it follows that the *heat of absorption of gases must always be greater than their heat of condensation.* This, indeed, is shown by comparing a couple of the numbers taken from the two preceding groups. For SO_2 and NH_3 the heats of absorption of the substances in the gaseous state, as well as their heats of solution when liquefied, have been experimentally determined. The following figures are taken from the tables:—

	SO_2	NH_3
Heat of absorption of gas . . .	7700 c	8430 c
Heat of solution of liquid . . .	1500	3400
Heat of condensation	6200 c	5030 c

That the thermal effect for many of the substances recorded

in the tables is very considerable is due to the fact that, in these cases, the solution of the substance in water is accompanied by the formation of a hydrate; as, for instance, on solution of SO_3, or by a decomposition, as in the case of $COCl_2$.

In the *third subdivision*, containing solid compounds of the non-metals, the thermal effect is generally *negative*, when there is neither hydrate formation (P_2O_5), nor complete decomposition (PCl_5) taking place; and from this characteristic it follows that the substance in solution goes from the solid into the liquid condition.

The thermal effect on solution of a substance in the liquid condition must always be greater than that of the same substance when crystallized; the difference constitutes the *heat of fusion*, which must always be positive. The tables give many examples of this, since the heats of solution have been measured for H_3PO_4, H_3PO_3, and H_3PO_2, in the liquid as well as in the crystallized condition, and at the same temperature, with the following results:—

	H_3PO_4	H_3PO_3	H_3PO_2
Acid (liquid)	5210 c	2940 c	2140 c
Acid (crystallized) . . .	2690	−130	−170
Heat of fusion	2520 c	3070 c	2310 c

2. The *fourth subdivision* includes the heats of solution of 200 compounds, the oxides, hydroxides, halides, and oxy-salts of 30 metals in all. From a closer comparison of all these numbers we are able to draw some conclusions of a more general character.

The heats of solution of *anhydrous salts* exhibit the following relations:—

(*a*) Anhydrous chlorides, bromides, iodides, and salts, which dissolve in water with *evolution of heat*, are able to form crystalline compounds with water (or are completely decomposed by it).

(*b*) Chlorides, bromides, iodides, and salts, which do not form crystalline compounds with water (nor are completely decomposed by it), dissolve in water with *absorption of heat.*

Thus the *first* of these two groups contains the *anhydrous halides* with *positive heats of solution;* these include compounds of Li, Ba, Sr, Ca, Mg, Al, Zn, Mn, Fe, Co, Ni, Cu, and Sn, which can also all form crystalline compounds with water. To this group belong, in addition, $CdCl_2$ and $CdBr_2$ with positive heats of solution and corresponding hydrates, whilst CdI_2 belongs to the other group with a negative heat of solution and without a corresponding hydrate. Compounds of gold show a similar relation; the heat of solution of $AuCl_3$ is positive, and the chloride gives a hydrate $AuCl_3 . 2H_2O$; for $AuBr_3$, on the other hand, it is negative, and there is no corresponding hydrate. An exception occurs in the case of NaCl and NaBr, the heats of solution of which are weakly negative, respectively -1180 c and -190 c; but these substances nevertheless form hydrates, the water in which is, however, very loosely bound; NaI, on the contrary, follows the rule.

The *second* of the two groups is composed of the anhydrous halides which do not form hydrates (or undergo decomposition), and of which the heats of solution are negative, as, for instance, the halides of K, Pb, Hg, Tl, and Ag, together with CdI_2 and $AuBr_3$, as well as the double halides of potassium with Pt, Pd, and Hg. For all these compounds the heat of solution is negative, usually very strongly so; as, for instance, $-20{,}200$ c for Tl_2Cl_2, and from $-10{,}000$ c to $-15{,}000$ c for the potassium halide compounds mentioned; for sodium platinichloride and bromide, on the other hand, it is, in accordance with rule *a*, positive, since these substances form hydrates.

Oxy-salts behave in a similar manner. *The salts of potassium* are for the most part anhydrous; thus chloric and bromic acids, dithionic, trithionic, and tetrathionic acids, nitric, sulphuric, dichromic, perchloric, and periodic acids all form potassium salts which are anhydrous, while with other bases these acids form, as a rule, hydrated salts. Potassium salts belong, therefore, to the second group of compounds, and their heats of solution are also strongly *negative;* the *carbonate* alone dissolves with evolution of heat, combines with water, and belongs to the first group.

Sodium salts have a greater affinity for water than potassium

salts; they are usually hydrated, and consequently many of the anhydrous sodium salts dissolve with evolution of heat, as, for instance, the carbonate, sulphate, phosphate, pyrophosphate, and borate, which consequently, according to rule, belong to the first group.

The anhydrous salts of the *magnesium group* all have a positive heat of solution, they form hydrates, and belong to the first group; whilst lead, thallium, and silver salts, which do not form hydrates, belong to the second group and dissolve with absorption of heat.

Hydrated salts ought, in accordance with the rules laid down, to have negative heats of solution; this, again, is usually the case, and will certainly always be so when the salt contains the maximum number of molecules of water which it, or similar salts, are able to take up.

3. *Regularity in the heat of solution of salts.*—A comparison between the heats of solution of allied salts leads to noteworthy results, some of which will now be considered.

Sulphates and nitrates of the K, Na, Tl, and *NH_4 group* show nearly equal differences between their heats of solution. Thus the tables give

R =	K	Na	Tl	NH_4
R_2SO_4 . . .	− 6,380 c	+ 460 c	− 8,280 c	− 2,370 c
$2RNO_3$ . . .	−17,040	−10,060	−19,940	−12,640
Difference . .	10,660 c	10,520 c	11,660 c	10,270 c

Sodium, potassium, and lithium.—The differences between the heats of solution of the halides of sodium and potassium show the following conformity:—

$$2NaCl - 2KCl = 6{,}520\text{ c} = 2 \times 3260\text{ c}$$
$$2NaBr - 2KBr = 9{,}780 = 3 \times 3260$$
$$2NaI - 2KI = 12{,}660 = 4 \times 3165$$
$$Na_2PtCl_6 - K_2PtCl_6 = 22{,}300 = 7 \times 3186$$
$$Na_2PtBr_6 - K_2PtBr_6 = 22{,}250 = 7 \times 3179$$
$$2LiCl - 2NaCl = 19{,}240 = 6 \times 3207$$

In the first group the differences between the heats of solution of chlorides, bromides, and iodides are in the ratio of 2 : 3 : 4; in the second group, where the values are equal to one another, we find the same constant but multiplied by 7. Similarly the difference between the heats of solution of the chlorides of lithium and sodium is a multiple of the same constant.

Lead, silver, and thallium.—From the values given later, in Chapter V., we can deduce the following heats of solution for the halides of these substances :—

$$\left.\begin{aligned} PbCl_2 - 2AgCl &= 24{,}900 \text{ c} = 4 \times 6225 \text{ c} \\ PbBr_2 - 2AgBr &= 30{,}180 \quad = 5 \times 6036 \\ PbI_2 - 2AgI &= 36{,}870 \quad = 6 \times 6145 \end{aligned}\right\}$$

$$\left.\begin{aligned} PbCl_2 - 2TlCl &= 13{,}400 \quad = 4 \times 3350 \\ PbBr_2 - 2TlBr &= 16{,}460 \quad = 5 \times 3292 \\ PbI_2 - 2TlI &= 19{,}730 \quad = 6 \times 3288 \end{aligned}\right\}$$

Of these values only the heats of solution of $PbCl_2$, $PbBr_2$, and 2TlCl were estimated by direct experiment; the others are arrived at by calculation; the agreement is, therefore, particularly noteworthy.

Magnesium, calcium, strontium, and barium.—The heats of solution of the halides show the following relation :—

$$\begin{aligned} MgCl_2 - CaCl_2 &= 18{,}510 \text{ c} = 6 \times 3085 \text{ c} \\ CaCl_2 - SrCl_2 &= 6{,}270 \quad = 2 \times 3135 \\ SrCl_2 - BaCl_2 &= 9{,}070 \quad = 3 \times 3023 \end{aligned}$$

For the corresponding hydrated salts we find

$$\begin{aligned} CaCl_2 . 6H_2O - SrCl_2 . 6H_2O &= 3160 \text{ c} = 1 \times 3160 \text{ c} \\ CaBr_2 . 6H_2O - SrBr_2 . 6H_2O &= 6130 \quad = 2 \times 3065 \end{aligned}$$

Copper, barium, and tin show the following differences :—

$$\begin{aligned} CuCl_2 - BaCl_2 &= 9010 \text{ c} = 3 \times 3003 \text{ c} \\ CuBr_2 - BaBr_2 &= 3270 \quad = 1 \times 3270 \\ CuCl_2 . 2H_2O - BaCl_2 . 2H_2O &= 9140 \quad = 3 \times 3047 \\ CuCl_2 . 2H_2O - SnCl_2 . 2H_2O &= 9580 \quad = 3 \times 3193 \end{aligned}$$

All the differences noted between the heats of solution of two related compounds would thus appear to be multiples of

a constant, equal to from 3000 c to 3200 c, and of a simple integer.

4. *Dependence of the heat of solution upon the molecular weight of the substance.*—For allied compounds the heat of solution appears to change uniformly with the atomic weight of the constituents. In the case of the halides of the alkaline earths corresponding to the formula RQ_2, where R is an atomic weight respectively of 24, 40, 87, and 137, whilst Q equals 35, 80, and 127, respectively, for Cl, Br, and I, *the heat of solution rises simultaneously with the atomic weight of the electro-negative radical Q, but decreases when the atomic weight R of the metal rises.* The heats of solution are as follows:—

RQ_2	R	Q = Cl	Q = Br	Q = I
MgQ_2	24	35,920 c	—	—
CaQ_2	40	17,410	24,510 c	27,690 c
SrQ_2	87	11,140	16,110	—
BaQ_2	127	2,070	4,980	—

A similar relation, namely, that the *heat of solution decreases when the atomic weight of the electro-positive radical of the compound increases*, is shown by the combinations R_2Cl_6 and RCl_4; their heats of solution are:—

R_2Cl_6	R	Heat of solution.	RCl_4	R	Heat of solution.
Al_2Cl_6	27	153,690 c	$SiCl_4$	28	69,290 c
P_2Cl_6	31	130,280	$TiCl_4$	50	57,870
Fe_2Cl_6	56	63,390	$SnCl_4$	118	29,920
As_2Cl_6	75	35,160			
Sb_2Cl_6	120	17,600			
Au_2Cl_6	197	8,900			

The members of the following group behave in a similar manner, in that the heats of solution decrease with an increase of atomic weight of the electro-positive radical in the molecule RQ_2; but at the same time, in contradistinction to that which

is observed in the preceding group, the heats of solution also decrease when Q increases.

RQ_2	R	Q = Cl	Q = Br	Q = I
ZnQ_2	65	15,630 c	15,030 c	11,310 c
CuQ_2	64	11,080	8,250	—
CdQ_2	112	3,010	440	−960
PbQ_2	207	−6,800	−10,040	—

From a comparison of these numbers it would appear that the heat of solution of a substance depends in a perfectly regular manner upon the atomic weights of the constituent elements, although no fixed rule can be laid down.

5. *Summary.*—Briefly, the relations observed between the heats of solution of halides and oxy-salts can be expressed as follows:—

(*a*) Anhydrous chlorides, bromides, iodides, and salts which dissolve in water with evolution of heat, form crystalline compounds with water (or are completely decomposed by it).

(*b*) Chlorides, bromides, iodides, and salts which do not form hydrates (nor are completely decomposed in aqueous solution) dissolve in water with absorption of heat.

(*c*) The heats of solution of hydrated halides and oxy-salts are negative when the salt has taken up its maximum amount of water.

(*d*) The thermal effect of hydrate formation is positive.

(*e*) The magnitude of the heat of solution depends upon the atomic weights of the constituent elements of the substance in the following manner:—

(1) For analogous halides with the same electro-negative element the heat of solution if positive is greater, if negative less, the lower the atomic weight of the metal; and

(2) For analogous compounds with the same electro-positive element the heat of solution

sometimes rises simultaneously with increase of atomic weight of the electro-negative element (which holds for Mg, Ca, Sr, Ba, Na); it sometimes falls with the same increase (valid for Zn, Cu, Cd, Au, Pb, Hg, Ag, Tl). Apparently the metals group themselves as light and heavy metals.

Although these results are drawn from a very large number of observations on heats of solution, it is, of course, possible that they may be modified by further researches.

Information respecting the probable heats of solution of many very sparingly soluble salts will be found in Part III., under the articles lead, thallium, mercury, and silver.

CHAPTER II

HEATS OF SOLUTION OF PARTIALLY DEHYDRATED SALTS, THEIR HEATS OF HYDRATION, AND CONSTITUTION

A. Numerical Results.

1. *Heat of total hydration.*—Among the results considered in the preceding chapter the heats of solution of a number of hydrated salts are to be found. For most of these the heat of solution of the corresponding anhydrous salt is also recorded, and the difference between these two numbers will therefore denote the thermal effect which takes place when the anhydrous salt unites with a definite number of water molecules to form the crystalline hydrate. Thus the heat of solution of 1 gram-molecule of $SrCl_2$ is 11,140 c, whilst for the gram-molecule $SrCl_2 . 6H_2O$, the value is -7500 c, and the difference between these two numbers, namely 18,640 c, is therefore the thermal effect due to the union of the anhydrous salt with 6 gram-molecules of water; that is to say, the *heat of hydration* of the anhydrous salt.

The heat of hydration arises as a matter of course partly from the affinity of the salt for water, partly from the latent heat of the water, since the water molecules change their state of liquid aggregation to become the constituents of a solid body. If we wish to give the thermal effect due to the union of a salt with water in the solid state, that is with ice, we must decrease the thermal effect by 1440 c for each molecule of water; then the value for $SrCl_2 . 6H_2O$ will be only 18,640 c $- 6 \times 1440$ c, or 10,000 c.

The heat of hydration varies considerably for different salts, being partly dependent upon the nature of the salt, partly

upon the number of molecules of combined water. In the table below is a summary of the heats of hydration of those salts of which the heats of solution were given in the tables of the preceding chapter. All values refer to a temperature of about 18° C., and to water in the liquid state.

TABLE 2.

HEAT OF TOTAL HYDRATION.

($MgCl_2$, $6H_2O$)	32,970 c	(Na_2PtCl_6, $6H_2O$)	19,170 c
($SrBr_2$, $6H_2O$)	23,330	(Na_2PtBr_6, $6H_2O$)	18,540
($SrCl_2$, $6H_2O$)	18,640	($K_2Mg(SO_4)_2$, $6H_2O$)	20,620
($CaCl_2$, $6H_2O$)	21,750	($K_2Zn(SO_4)_2$, $6H_2O$)	19,810
($CoCl_2$, $6H_2O$)	21,190	($K_2Cu(SO_4)_2$, $6H_2O$)	22,970
($NiCl_2$, $6H_2O$)	20,330		
($MnCl_2$, $4H_2O$)	14,470 c	($K_2Mn(SO_4)_2$, $4H_2O$)	12,820 c
($FeCl_2$, $4H_2O$)	15,150	(CaN_2O_6, $4H_2O$)	11,200
($CdBr_2$, $4H_2O$)	7,730	(SrN_2O_6, $4H_2O$)	7,680
($BaBr_2$, $2H_2O$)	9,110 c	($SnCl_2$, $2H_2O$)	5,720 c
($BaCl_2$, $2H_2O$)	7,000	(NaI, $2H_2O$)	5,230
($CuCl_2$, $2H_2O$)	6,870	(NaBr, $2H_2O$)	4,520
($AuCl_3$, $2H_2O$)	6,140	($CdCl_2$, $2H_2O$)	5,290
(Na_2HPO_4, $12H_2O$)	28,470 c	($CuSO_4$, $5H_2O$)	18,550 c
($Na_4P_2O_7$, $10H_2O$)	23,520	($MnSO_4$, $5H_2O$)	13,750
(Na_2CO_3, $10H_2O$)	21,800	($CdSO_4$, $\frac{8}{3}H_2O$)	8,080
(Na_2SO_4, $10H_2O$)	19,220	($Na_2S_2O_6$, $2H_2O$)	6,280
($MgSO_4$, $7H_2O$)	24,080	(K_2CO_3, $\frac{3}{2}H_2O$)	6,870
($ZnSO_4$, $7H_2O$)	22,690	(Li_2SO_4, H_2O)	2,640

The foregoing numbers give the total heats of hydration corresponding to the combination of the anhydrous salt with the maximum amount of water with which it forms the normal hydrate. The question now arises: Can any difference be detected in the thermal effect due to the addition of the separate molecules of water, and will this knowledge eventually give us an insight into the constitution of the normal hydrated salts?

2. *Heat of partial hydration.*—In order to gain information as to the strength with which the individual molecules of water are bound in crystalline hydrates, it was necessary to prepare

partially dehydrated salts and then to measure their heats of solution. The dehydration was carried out in a large, well-ventilated drying apparatus, specially constructed for the purpose, and in which the temperature could be accurately regulated. The finely powdered salt was placed upon a flat platinum plate, and the drying was continued for a considerable period at a constant temperature; each plate contained a known amount of salt. By weighing from time to time the progress of dehydration could be controlled; and when the weight showed that the required number of molecules of water had been driven off, the salt was analyzed, and then the heat of solution per gram-molecule in 400 gram-molecules of water was measured at the usual temperature of 18° C. It is hardly possible to carry out the dehydration so as to obtain a salt with the exact complement of molecules of water required; but by interpolation the heats of solution can be calculated for the salt with whole numbers of water molecules. In vol. iii. of *Therm. Unters.*, pp. 115–181, are found all particulars relating to 300 calorimetric experiments; here we shall only give the results which were obtained on calculating the heats of solution of salts containing whole numbers of water molecules.

TABLE 3.

HEAT OF PARTIAL HYDRATION.

(*a*) *Salts with an Even Number of Molecules of Water.*

1. DI-SODIUM HYDROGEN PHOSPHATE, $Na_2HPO_4 . 12H_2O$.

Salt.	Heat of solution.	Heat of partial hydration.
Na_2HPO_4	+ 5,640 c	
$Na_2HPO_4 . 2H_2O$	− 390	6,030 c = 2 × 3015 c
$Na_2HPO_4 . 7H_2O$	−11,640	11,250 = 5 × 2250
$Na_2HPO_4 . 12H_2O$	−22,830	11,190 = 5 × 2238

2. SODIUM PYROPHOSPHATE, $Na_4P_2O_7 . 10H_2O$.

$Na_4P_2O_7$	+11,850 c	
$Na_4P_2O_7 . H_2O$	+ 9,380	2,470 c = 1 × 2470 c
$Na_4P_2O_7 . 2H_2O$	+7,030	2,350 = 1 × 2350
$Na_4P_2O_7 . 5H_2O$	+ 50	6,980 = 3 × 2327
$Na_4P_2O_7 . 10H_2O$	−11,670	11,720 = 5 × 2344

3. Sodium Sulphate, $Na_2SO_4 . 10H_2O$.

Salt.	Heat of solution.	Heat of partial hydration.
Na_2SO_4	+ 460 c	
$Na_2SO_4 . H_2O$	− 1,900	2360 c = 1 × 2360 c
$Na_2SO_4 . 2H_2O$	− 3,740	1840 = 1 × 1840
$Na_2SO_4 . 5H_2O$	− 9,380	5640 = 3 × 1880
$Na_2SO_4 . 10H_2O$	−18,760	9380 = 5 × 1876

4. Sodium Carbonate, $Na_2CO_3 . 10H_2O$.

Na_2CO_3	+ 5,636 c		
$Na_2CO_3 . H_2O$	+ 2,254	3382 c	= 1 × 3382 c
$Na_2CO_3 . 2H_2O$	+ 43	2211	= 1 × 2211
$Na_2CO_3 . 3H_2O$	− 2,067	2110, 2135	4245 = 2 × 2122
$Na_2CO_3 . 4H_2O$	− 4,202	2436, 1774	4210 = 2 × 2105
$Na_2CO_3 . 5H_2O$	− 6,638	2353, 1858	4211 = 2 × 2105
$Na_2CO_3 . 6H_2O$	− 8,412	1764, 1773	3537 = 2 × 1768
$Na_2CO_3 . 7H_2O$	−10,765		
$Na_2CO_3 . 8H_2O$	−12,623		
$Na_2CO_3 . 9H_2O$	−14,387		
$Na_2CO_3 . 10H_2O$	−16,160		

5. Sodium Platinichloride, $Na_2PtCl_6 . 6H_2O$.

Na_2PtCl_6	+ 8,540 c		
$Na_2PtCl_6 . H_2O$	+ 4,210	4330 c, 4290	= 2 × 4310 c
$Na_2PtCl_6 . 2H_2O$	− 80		
$Na_2PtCl_6 . 3H_2O$	− 2,610	2530, 2590	= 2 × 2560
$Na_2PtCl_6 . 4H_2O$	− 5,200		
$Na_2PtCl_6 . 5H_2O$	− 7,920	2720, 2710	= 2 × 2715
$Na_2PtCl_6 . 6H_2O$	−10,630		

6. Strontium Chloride, $SrCl_2 . 6H_2O$.

$SrCl_2$	+11,140 c		
$SrCl_2 . H_2O$	+ 5,880	5260 c	= 1 × 5260 c
$SrCl_2 . 2H_2O$	+ 2,077	3803	= 1 × 3803
$SrCl_2 . 3H_2O$	− 387	2464, 2449	= 2 × 2456
$SrCl_2 . 4H_2O$	− 2,836		
$SrCl_2 . 5H_2O$	− 5,164	2328, 2336	= 2 × 2332
$SrCl_2 . 6H_2O$	− 7,500		

7. Barium Chloride, $BaCl_2 . 2H_2O$.

$BaCl_2$	+2070 c		
$BaCl_2 . H_2O$	−1100	3170 c	= 1 × 3170 c
$BaCl_2 . 2H_2O$	−4930	3830	= 1 × 3830

8. Strontium Bromide, $SrBr_2 . 6H_2O$.

$SrBr_2$	+16,110 c		
$SrBr_2 . H_2O$	+ 9,960	6150 c	= 1 × 6150 c
$SrBr_2 . 2H_2O$	+ 6,160	3800	= 1 × 3800
$SrBr_2 . 3H_2O$	+ 3,060	3100, 3100, 3160	= 3 × 3120
$SrBr_2 . 4H_2O$	− 40		
$SrBr_2 . 5H_2O$	− 3,200	4020	= 1 × 4020
$SrBr_2 . 6H_2O$	− 7,220		

9. POTASSIUM MANGANOUS SULPHATE, $K_2Mn(SO_4)_2 . 4H_2O$.

Salt.	Heat of solution.	Heat of partial hydration.
$K_2Mn(SO_4)_2$	+ 6380 c	
$K_2Mn(SO_4)_2 . H_2O$	+ 1760	4620 c = 2 × 4645 c
$K_2Mn(SO_4)_2 . 2H_2O$	− 2910	4670
$K_2Mn(SO_4)_2 . 3H_2O$	− 4600	1690 = 2 × 1762
$K_2Mn(SO_4)_2 . 4H_2O$	− 6435	1835

10. POTASSIUM COPPER SULPHATE, $K_2Cu(SO_4)_2 . 6H_2O$.

$K_2Cu(SO_4)_2$	+ 9,400 c	
$K_2Cu(SO_4)_2 . H_2O$	+ 4,100	5300 c = 2 × 5305 c
$K_2Cu(SO_4)_2 . 2H_2O$	− 1,210	5310
$K_2Cu(SO_4)_2 . 3H_2O$	− 4,290	3080 = 2 × 2995
$K_2Cu(SO_4)_2 . 4H_2O$	− 7,200	2910
$K_2Cu(SO_4)_2 . 5H_2O$	−10,460	3260 = 2 × 3185
$K_2Cu(SO_4)_2 . 6H_2O$	−13,570	3110

11. POTASSIUM MAGNESIUM SULPHATE, $K_2Mg(SO_4)_2 . 6H_2O$.

$K_2Mg(SO_4)_2$	+10,600 c	
$K_2Mg(SO_4)_2 . H_2O$	+ 6,122	4478 c
$K_2Mg(SO_4)_2 . 2H_2O$	+ 741	5381
$K_2Mg(SO_4)_2 . 3H_2O$	− 2,038	2779
$K_2Mg(SO_4)_2 . 4H_2O$	− 5,160	3122
$K_2Mg(SO_4)_2 . 5H_2O$	− 7,954	2794
$K_2Mg(SO_4)_2 . 6H_2O$	−10,024	2070

12. POTASSIUM ZINC SULPHATE, $K_2Zn(SO_4)_2 . 6H_2O$.

$K_2Zn(SO_4)_2$	+ 7,909 c	
$K_2Zn(SO_4)_2 . H_2O$	+ 4,055	3854 c
$K_2Zn(SO_4)_2 . 2H_2O$	+ 446	3609
$K_2Zn(SO_4)_2 . 3H_2O$	− 2,634	3080
$K_2Zn(SO_4)_2 . 4H_2O$	− 5,010	2376
$K_2Zn(SO_4)_2 . 5H_2O$	− 9,176	4166
$K_2Zn(SO_4)_2 . 6H_2O$	−11,900	2724

13. $CaCl_2 . 6H_2O$. 14. $MgCl_2 . 6H_2O$.

Heat of Solution of the Salt.

n	$CaCl_2 . nH_2O$	m	$MgCl_2 . mH_2O$
0·0	17,410 c	0·0	35,920 c
1·67	10,800	3·05	14,871
1·98	10,036	4·51	8,360
2·75	6,927	4·61	7,781
3·49	3,752	5·05	6,181
3·76	2,971	6·11	2,950
6·07	−4,340		

(*b*) *Salts with an Uneven Number of Molecules of Water.*

15. Magnesium Sulphate, $MgSO_4 . 7H_2O$.

Salt.	Heat of solution.	Heat of partial hydration.
$MgSO_4$	20,280 c	
$MgSO_4 . H_2O$	13,300	6980 c
$MgSO_4 . 2H_2O$	11,050	2250
$MgSO_4 . 3H_2O$	7,490	3560
$MgSO_4 . 4H_2O$	4,240	3250
$MgSO_4 . 5H_2O$	2,010	2230
$MgSO_4 . 6H_2O$	− 100	2110
$MgSO_4 . 7H_2O$	3,800	3700

16. Zinc Sulphate, $ZnSO_4 . 7H_2O$.

$ZnSO_4$	18,430 c	
$ZnSO_4 . H_2O$	9,950	8480 c
$ZnSO_4 . 2H_2O$	7,670	2280
$ZnSO_4 . 3H_2O$	5,270	2400
$ZnSO_4 . 4H_2O$	3,500	1770
$ZnSO_4 . 5H_2O$	1,300	2200
$ZnSO_4 . 6H_2O$	− 840	2140
$ZnSO_4 . 7H_2O$	−4,260	3420

17. Copper Sulphate, $CuSO_4 . 5H_2O$.

$CuSO_4$	15,800 c	
$CuSO_4 . H_2O$	9,330	6470 c
$CuSO_4 . 2H_2O$	6,160	3170
$CuSO_4 . 3H_2O$	2,810	3350
$CuSO_4 . 4H_2O$	630	2180
$CuSO_4 . 5H_2O$	−2,750	3380

18. Manganous Sulphate, $MnSO_4 . 5H_2O$.

$MnSO_4$	13,790 c	
$MnSO_4 . H_2O$	7,810	5980 c
$MnSO_4 . 2H_2O$	6,240	1570
$MnSO_4 . 3H_2O$	4,150	2090
$MnSO_4 . 4H_2O$	2,240	1910
$MnSO_4 . 5H_2O$	40	2200

19. Cadmium Sulphate, $3CdSO_4 . 8H_2O$.

$3CdSO_4$	32,220 c	
$3CdSO_4 . 3H_2O$	18,150	14,070 c = 3 × 4690 c
$3CdSO_4 . 8H_2O$	7,980	10,170 = 5 × 2034

20. Potassium Carbonate, $2K_2CO_3 . 3H_2O$.

$2K_2CO_3$	12,980 c	
$2K_2CO_3 . H_2O$	8,560	4420 c = 1 × 4420 c
$2K_2CO_3 . 3H_2O$	− 760	9320 = 2 × 4660

B. General Character of the Heat of Hydration.

In the table above, which contains researches on the heats of partial hydration of 20 salts, a distinction is made between salts with an even and those with an odd number of molecules of water. The reason of this is that in the case of the first-mentioned salts the thermal effects corresponding to the addition of the individual molecules of water are far more uniform, and this can be explained if we suppose that in the first group the molecules of water are symmetrically arranged around the nucleus of the salt; in the second case, on the other hand, the addition of the first molecule of water, which is accompanied by a considerable thermal effect, produces a disturbance in the symmetry of the molecule. I shall therefore refer to each group separately.

(*a*). *Salts with an even number of molecules of water.*—From the numbers given above it is evident that the individual molecules of water in the hydrated salts are bound with unequal strength; *sodium pyrophosphate* alone appears to have *all* 10 *molecules bound in the same manner*, and with a strength corresponding to 2352 c for each gram-molecule of water. It is true that the first molecule seems to have a slightly greater thermal effect (2470 c); but this may be accidental.

Di-sodium hydrogen phosphate has a total heat of hydration of 28,470 c, which, distributed between the 12 molecules of water, gives a mean value of 2370 c, almost the same as in the case of the pyrophosphate; but the separate molecules are not bound in the same manner; the first two, which give 3015 c for each gram-molecule, are more strongly bound than each of the following 10, which are all bound with the same strength, namely 2244 c. This is altogether in accordance with the observation that the salt very quickly loses 10 molecules of water by standing over lime, leaving a salt with 2 molecules of water; and, moreover, it is this last-mentioned salt which is formed, without separation of water, when phosphoric acid is treated with caustic soda, thus

$$2NaOH + H_3PO_4 = Na_2HPO_4 . 2H_2O.$$

Curiously enough, the well-known salt $Na_2HPO_4 . 7H_2O$ is not indicated by the heat of hydration; thus for the last 5, and for the 5 preceding, molecules of water the heats of hydration are equal, namely, 11,190 c and 11,250 c.

Sodium sulphate with 10 molecules of water agrees very closely with the preceding salts; but its heat of hydration is rather small. The *first* molecule of water has a heat of hydration of 2360 c, which is equal to that found for each of the 10 molecules in the pyrophosphate. But the rest of the water is even more weakly bound, and the heat of hydration is the same for each of the following 9 molecules, namely 1873 c; there is no indication of the formation of any other hydrates. The first-mentioned salt, $Na_2SO_4 . H_2O$, is the one which separates when a concentrated solution of the sulphate with 10 molecules of water, made at 30°, is warmed; the salt is usually taken as anhydrous, but contains 1 molecule of water (see *l.c.*, p. 122).

Sodium carbonate with 10 molecules of water shows rather more complex behaviour; an investigation of the heats of hydration of each of the 10 molecules was therefore deemed advisable. From the values obtained we see that the addition of the first molecule entails a comparatively large evolution of heat, namely 3380 c; for the 7 following molecules the average value is 2125 c, and finally the last two molecules develop equal amounts of heat, viz. 1768 c. But the 7 molecules do not each show the same heat of hydration; the following numbers, taken from the preceding table,

2nd	3rd	4th	5th	6th	7th	8th mol. water
2211 c	2110 c	2135 c	2436 c	1774 c	2353 c	1858 c
	4245 c		4210 c		4211 c	

show that although the thermal effect is unequal for the single molecules, yet nevertheless the sum of two consecutive numbers is equal; thus the 3rd and 4th, the 5th and 6th, or the 7th and 8th, gram-molecules of water taken in pairs give nearly identical thermal effects. Whether this points to the existence of salts with 4, 6, and 8 molecules of water, or whether it is due to an irregularity in the dehydration of the salt, is difficult to

decide; but very possibly we have here an indication of a phenomenon of even greater importance, and which is observed still more plainly in the three following salts.

Sodium platinichloride, *potassium copper sulphate*, and *potassium manganous sulphate*, with respectively 6 and 4 molecules of water, show with absolute certainty that *when pairs of molecules of water are taken up they develop nearly equal heats of hydration;* and, moreover, the first pair in all three salts shows a greater heat of hydration than each of the following. The natural explanation of this phenomenon is that the *molecules of water are symmetrically arranged in pairs around the nucleus of the salt*, so that the structure of the crystallized salt is symmetrical with respect to the water molecules concerned.

Strontium chloride, *strontium bromide*, and *barium chloride*.—The heats of hydration of these salts are unequal for the first 2 molecules of water; but for the remainder strontium chloride presents the above-mentioned phenomenon, namely, that the 4 following molecules are taken up in pairs with the same thermal effect. This behaviour is consistent with the constitution which, after thorough investigation, I have proposed for hydrochloric acid and its salts (*Therm. Unters.*, ii. 430–444). According to this, hydrogen chloride is the anhydride of an acid $HOClH_2$, of which the normal salts of the divalent metals correspond to the formula $R(OClH_2)_2$, thus $CuCl_2 . 2H_2O$, $BaCl_2 . 2H_2O$. It is these two molecules of water that are taken up by the anhydrous salt with so great an evolution of heat, whilst the following molecules are added on symmetrically and in pairs. It is noteworthy, in addition, that the other molecules of water in all three salts are taken up with an equal thermal effect, respectively 3803, 3800, and 3830 c.

Potassium magnesium sulphate and *potassium zinc sulphate* with 6 molecules of water resemble the corresponding salts of copper and manganese; but unfortunately they cannot be prepared in so pure a state as the copper salt, which is precipitated in small, well-formed crystals on mixing solutions containing copper sulphate and potassium nitrate of equivalent concentrations; these, after being separated from the mother

liquor by means of a filter pump, and washed with a cold concentrated solution of the salt, are quite pure. The other two salts, on the contrary, owing to their greater solubility, and to the ease with which they decompose into their constituent salts in concentrated solution, cannot be formed in the above-mentioned manner, and they therefore always contain a slight excess of one or the other salt. Also there is a greater uncertainty as to the dehydration of these salts than is the case with the copper salt. Experiments with these two double sulphates cannot therefore be regarded as so reliable as the preceding examples; but it is noticeable, nevertheless, that the heat of hydration is greater for the first 2 molecules of water than for those following. It will also readily be observed that the sum of the heats of hydration of the last 4 molecules of water is equal for the zinc and for the copper salt, namely, 12,346 c and 12,360 c respectively.

The chlorides of calcium and *magnesium* have, as is well known, a very strong attraction for water, which also finds expression in their very large heats of hydration, respectively 21,750 c and 32,970 c. Magnesium chloride adds on the first 3 molecules of water with a heat evolution of 21,050 c, or an average of 7000 c for each gram-molecule; this is the greatest heat of hydration that has been observed. The dehydration of the crystallized salt containing 6 molecules of water is attended with great uncertainty, and for magnesium chloride it cannot be carried beyond 3 molecules without partial hydrolysis of the salt. The experimental results are given above; but I do not regard them as sufficiently trustworthy to be available for determining the heat of hydration by interpolation of the individual molecules of water.

(*b*) *Salts with an uneven number of molecules of water.*—Of the salts belonging to this group I have investigated the sulphates of Mg, Zn, Cu, and Mn (Nos. 15–18), and also the carbonates of cadmium and potassium. The experiments gave the usual result for all the sulphates concerned, namely, that the addition of the first molecule of water is attended by a great evolution of heat, varying between 8440 c for zinc sulphate and 4690 c for cadmium sulphate ($CdSO_4 . \frac{5}{3}H_2O$), which is in

complete agreement with the fact that the dehydration of the sulphates $RSO_4 . H_2O$ takes place only on strong heating, whilst the crystallized sulphates lose their water molecules very easily until they arrive at the monohydrated stage. Besides this, we also notice here many examples of the above-mentioned characteristic, namely, that the heats of addition to a salt of two consecutive molecules of water are equal. The magnitude of the heat of hydration for the separate molecules is on the whole lower than has been observed for the rest of the salts, since in 11 cases it is about 2181 c, in 7 cases about 3404 c, and in 2 cases it amounts only to 1670 c.

It is curious that potassium carbonate does not take up a larger number of molecules of water, notwithstanding the fact that the heat of hydration for each of the 3 molecules is very high.

The results of the preceding researches can be briefly compared as follows:—

(*a*) The heat of hydration of hydrated salts is equal to the difference between their heats of solution and those of the corresponding anhydrous salts, and is equivalent to the amount of heat-change which takes place when the anhydride unites with the number of water molecules which the hydrate contains.

(*b*) The magnitude of the heat of hydration varies considerably, and is dependent partly on the nature of the salt, partly on the number of water molecules which are taken up; the latent heat of the latter naturally increases the real heat of hydration in proportion to the amount of water, namely, by 1440 c for each added gram-molecule of water.

(*c*) The distribution of the heat of hydration between the individual molecules of water is as a rule very different; for one only out of the 20 salts investigated, namely, the pyrophosphate of sodium, $Na_4P_2O_7 + 10H_2O$, does it appear that all 10 molecules have a uniform function, since the thermal effect is the same for each molecule taken up by the anhydrous salt—that is, 2352 c.

(*d*) The first, and partly also the second, molecule of water taken up by an anhydrous salt produces as a rule a stronger,

sometimes a very much stronger, thermal effect than each of the subsequent molecules. This is in complete accordance with the observation that the first, and sometimes also the second, molecule of water is more strongly bound than are the remaining molecules, and that a higher temperature is required for dehydration. This property is especially conspicuous in the sulphates of the magnesium group, in which the heat of hydration for the first molecule of water is also very considerable, namely, from 6000 to 8000 c.

(*e*) The thermal effect on addition of the remaining water molecules also shows certain analogies for different salts. If from the 20 salts investigated we omit the 4 salts (Nos. 11–14), in which the heat of partial hydration cannot be accurately estimated, there remain 100 determinations of the heats of partial hydration of the other 16 salts; if we deduct 16 of these, which relate to the first and partly to the second molecules of water in 11 salts, there remain 84 determinations. It now appears that 45 of these—that is, over a half—give values which approximate to that just mentioned for the heat of partial hydration of sodium pyrophosphate, namely 2352 c, and fall between 2100 c and 2490 c; further, that 17, or $\frac{1}{5}$ of the total number of estimations, are values between 1760 and 1860 c, while the remaining 22 (or $\frac{1}{4}$) lie between 3000 and 3800 c.

(*f*) In many cases it would appear that the heat of partial hydration is equal for two consecutive molecules of water. This is very noticeable in the salts Nos. 5, 9, and 10, in which the 1st and 2nd, the 3rd and 4th, and the 5th and 6th molecules have equal heats of hydration, and undoubtedly suggests that these salts are of symmetrical configuration. A somewhat similar property is seen in salt No. 4, where the sum of the heats of hydration of consecutive molecules of water appears to be a constant magnitude, and may be explained in the same way.

CHAPTER III

INFLUENCE OF THE AMOUNT OF WATER UPON THE HEAT OF SOLUTION—HEAT OF DILUTION OF AQUEOUS SOLUTIONS

In a preceding chapter the thermal effect due to the solution of substances in water was described, and the results of numerous series of determinations have been given; but the numbers quoted apply only to solutions containing that amount of water which is specified in each particular case. As a matter of fact, the thermal effect due to the solution of substances in water is not a constant magnitude, since it is not only dependent upon the nature of the dissolved substance, but is influenced also to a great extent by the amount of water present, as well as by its temperature; we shall now attempt to throw light on the former of these two influences.

Just as the researches on the heat of hydration of hydrated salts gave us an insight into the constitution of the salt, since they showed that the molecules of water which the salt is able to take up are differently bound, corresponding to the property which the salt has of forming several hydrates, so the following researches on the change of the heat of solution with varying amounts of water give us an insight into the nature of the solutions, and more especially afford information as to whether definite hydrates are formed in aqueous solution. When this is so the change of thermal effect with the amount of water must show certain fixed points, indicating the hydrates formed; in the opposite case the thermal effect must, on the other hand, vary as a regular, continuous function of the amount of water.

In carrying out this very extensive research, which comprises over 400 calorimetric experiments, the substance concerned was either dissolved in varying amounts of water, or a given solution was diluted with a known amount of water, and the thermal effect produced was measured. The experiments give the thermal effects due to the formation of solutions ranging from the greatest concentration (often for the anhydrous substance) to a degree of dilution which, according to the nature of the substance under consideration, is equal to 200, 400, 800, and 1600 molecules of water to 1 molecule of substance. The research treats of the following substances:—

Acids and Alkalies.

Sulphuric acid.	Formic acid.	Hydriodic acid.
Nitric acid.	Tartaric acid.	Potassium hydroxide.
Ortho-phosphoric acid.	Hydrochloric acid.	Sodium hydroxide.
Acetic acid.	Hydrobromic acid.	Ammonia.

Oxy-salts.

Sodium sulphate.	Sodium nitrate.	Potassium acetate.
Ammonium sulphate.	Ammonium nitrate.	Sodium acetate.
Magnesium sulphate.	Strontium nitrate.	Ammonium acetate.
Zinc sulphate.	Lead nitrate.	Zinc acetate.
Manganous sulphate.	Magnesium nitrate.	Potassium carbonate.
Copper sulphate.	Manganous nitrate.	Sodium carbonate.
Potassium hydrogen sulphate.	Zinc nitrate.	Ammonium hydrogen carbonate.
Sodium hydrogen sulphate.	Copper nitrate.	Ammonium tartrate.
Ammonium hydrogen sulphate.		

Halides.

Sodium chloride.	Magnesium chloride.	Copper chloride.
Ammonium chloride.	Zinc chloride.	Potassium bromide.
Calcium chloride.	Nickel chloride.	Sodium iodide.

It is evident from the preceding list that all the substances

investigated are readily soluble in water, a condition which the nature of the problem necessitates.

A. Heats of Solution and of Dilution of Acids and Alkalies.

Numerical and Theoretical Results.

1. *Sulphuric acid.*—The thermal effect due to the solution of sulphuric acid in water has been investigated over a large range of dilution, from the anhydride SO_3 up to the acid with 1600 molecules of water to 1 molecule of anhydride. There exist, as is well known, three crystalline hydrates, $2SO_3 + H_2O$, $SO_3 + H_2O$, and $SO_3 + 2H_2O$; but these can also be obtained as *liquids* at the temperature of the experiment, namely 18°, and it was in this condition that they were investigated.

Experiments have shown that the thermal effect due to the solution of sulphuric acid in water rises with the amount of water, so that for every increase in the amount of water there is an increased development of heat. If we express these results graphically, we find that they give a regular curve, resembling very closely a rectangular hyperbola. Further investigation shows also that the heat of solution in water of the hydrate H_2SO_4 can be approximately expressed by the formula

$$(H_2SO_4, nH_2O) = \frac{n \times 17{,}860\,c}{n + 1{\cdot}7983}.$$

The following table contains the experimental results of the whole series of estimations, together with the formulæ deduced from the numbers. The thermal effect which is due to the formation of the hydrates H_2SO_4 and $H_2S_2O_7$ starting from the anhydride is also given.

TABLE 4.

(H_2SO_4, nH_2O).

n	Results of experiment.	Calculated according to the formula $\frac{n \times 17{,}860\ c}{n + 1{\cdot}7983}$	Difference.
1	6,379 c	6,382 c	− 3 c
2	9,418	9,404	+ 14
3	11,137	11,167	− 30
4	—	12,320	—
5	13,108	13,135	− 27
9	14,952	14,886	+ 66
19	16,256	16,315	− 59
49	16,684		−544
99	16,858		−683
199	17,065		−636
·399	17,313		−467
799	17,641		−180
1599	17,857	17,840	+ 17

$(SO_3, H_2O) = 21{,}320$ c $(H_2S_2O_7, H_2O) = 18{,}620$ c
$(2SO_3, H_2O) = 24{,}020$ $(H_2SO_4, SO_3) = 2{,}700$

It is evident from the figures above that the evolution of heat is very considerable; namely, for the three hydrates—

$(SO_3, Aq) = 21{,}320\ c + 17{,}860\ c = 39{,}180\ c$
$\frac{1}{2}(H_2S_2O_7, Aq) = 39{,}180 - \frac{1}{2}24{,}020 = 27{,}170$
$(H_2SO_4, Aq) = 39{,}180 - 21{,}320 = 17{,}860$

The evolution of heat decreases considerably for each successive molecule of water. For example, for 1 gram-molecule of the anhydride we have the following values for each gram-molecule of water :—

1st	2nd	3rd	4th mol. H_2O
21,320 c	6380 c	3040 c	1720 c, etc.

We also see from the tables that the evolution of heat due to mixing 1 gram-molecule of H_2SO_4 with increasing amounts

of water agrees accurately, for all values of n between 1 and 19 which have been investigated, with the results calculated by means of the formula given, and that *within these limits of dilution there is no other hydrate in solution but ordinary* H_2SO_4. Furthermore, we note the peculiar circumstance that for values of n between 49 and 799 the observed thermal effects all fall considerably below those calculated according to the formula, whilst the agreement once more becomes apparent at still greater dilution. It is not easy to find any explanation of this behaviour, except in supposing that the formula used is only an approximate one.

If we insert $n = -1$ in the formula, we should obtain the thermal effect due to the dissociation of the hydrate H_2SO_4 into SO_3 and H_2O; for this reaction the above experimental results give $-21{,}320$ c, which is a very close approximation to the value required by the formula, namely $-22{,}372$ c. On the other hand, if we put $n = -0{\cdot}5$ the formula gives us a value of -6878 c, and for the dissociation of $2H_2SO_4$ into $H_2S_2O_7$ and H_2O, a value of $-13{,}756$ c while the experimental results give $-18{,}620$ c for this reaction. We thus have here a decided indication that the molecule $H_2S_2O_7$ really is a definite hydrate, which on solution in water is converted into H_2SO_4; the latter is therefore the *only hydrate present in aqueous solution.*

2. *Nitric acid.*—This acid appears on the whole to agree very closely with sulphuric acid. Experiments were carried out in which the amount of water varied from 0·5 to 320 molecules to 1 molecule of HNO_3. Here again the increasing evolution of heat can be expressed as a very close approximation to the hyperbolic function

$$(HNO_3, nH_2O) = \frac{n \times 8974 \text{ c}}{n + 1{\cdot}737},$$

as will be seen from the following table :—

TABLE 5.

(HNO_3, nH_2O).

n	Results of experiment.	Calculated according to the formula $\frac{n \times 8974\ c}{n + 1{\cdot}737}$	Difference.
0·5	2005 c	2008 c	− 3 c
1	3285	3285	0
1·5	4160	4160	0
2	—	4808	—
2·5	5276	5301	− 25
3	5710	5690	+ 20
4	—	6266	—
5	6655	6668	− 3
10	7318	7646	− 328
20	7458	—	—
40	7436	—	—
80	7421	—	—
100	7439	—	—
160	7450	—	—
320	7493	8827	−1366

The results calculated from the formula are in complete agreement with those derived from experiment, until the quantity of water amounts to 5 molecules for each molecule of HNO_3, and there can therefore be no doubt that the solution contains only the molecule HNO_3. But as soon as the amount of water rises above 5 molecules, we see from the table that the observed evolution of heat falls considerably below the calculated value. Exactly similar behaviour was shown by sulphuric acid when the amount of water rose above 19 molecules for 1 molecule of H_2SO_4; but with nitric acid the difference appears to be much greater.

It is also noteworthy that the thermal effect on dilution of nitric acid with water has already reached its *maximum when there are* 20 *molecules of water to* 1 *molecule of* HNO_3, *and that beyond this no further change takes place;* thus the mean value of the 6 degrees of dilution, from 20 to 320 gram-molecules of

water, is 7440 c, while the experimental value for 20 gram-molecules of water is 7458 c. It follows from this that a nitric acid solution which contains 20 molecules of water will give no thermal effect on mixing with more water; while the thermal effect for sulphuric acid increases with the degree of dilution.

3. *Phosphoric acid.*—The heat of dilution of this acid is given in the table below, and refers to the acid as a *liquid;* while for the crystallized acid the value is 2520 c lower, which corresponds to the heat of fusion (see p. 54).

TABLE 6.

n	H_3PO_4, nH_2O
1	1741 c
3	3298
9	4509
20	4938
50	5169
100	5269
200	5355

The thermal effect is here again a hyperbolic function of the amount of water, but is not in other respects remarkable.

4. *Hydrochloric, hydrobromic, and hydriodic acids.*—The following table contains the heats of absorption of these acids in increasing amounts of water. In carrying out the experiments the heat of absorption in a large amount of water (300–500 gram-molecules) was measured directly, and then the heat of dilution was determined when the acids at different degrees of concentration were mixed with water; the most concentrated solutions had the composition $HCl + 2{\cdot}62H_2O$, $HBr + 2{\cdot}21H_2O$, and $HI + 2{\cdot}86H_2O$. The heats of absorption found in the tables refer to whole numbers of water molecules; these values are calculated by interpolation from the experimental results.

TABLE 7.

n	(HCl, nH_2O)	(HBr, nH_2O)	(HI, nH_2O)
1	(5,375 c)		
2	11,365	(13,860 c)	(12,540 c)
3	13,362	15,910	14,810
5	14,959	17,620	17,380
6	—	18,250	—
10	16,157	19,100	18,580
20	16,756	19,470	18,990
50	17,115	19,820	19,140
100	17,235	19,910	19,180
300	17,315	—	—
500	—	19,940	19,210

The thermal effect is in all three cases a hyperbolic function of n, and we should therefore be justified in assuming that, as in the case of sulphuric and nitric acids, it could be expressed by the formula

$$R = \frac{n}{n+r} C;$$

but this is, however, not the case. The special researches, with respect to which I must refer the reader to *Thermochemische Untersuchungen*, vol. iii. pp. 11 and 71, which gives the explanation and calculations of the experimental results, show that the thermal effect, as far as *hydrogen chloride* is concerned, can be satisfactorily expressed by the formula

$$(HCl, (m+1)\, H_2O) = \frac{m}{m+1}\ 11{,}980\ \text{c} + 5375\ \text{c}.$$

For $m = 0$, and $n = 1$, the formula gives the value

$$(HCl, H_2O) = 5375\ \text{c},$$

which is the *thermal effect due to the absorption of* 1 *gram-molecule of HCl in* 1 *gram-molecule of* H_2O; while when $m = \infty$,

$$(HCl, Aq) = 17{,}355\ \text{c},$$

which is the *maximum* heat of absorption for a gram-molecule of *HCl*; by experiment we find 17,315 c for 300 gram-molecules of water.

The formula referred to is also significant, since it supports the view, already established in a number of different ways (*Therm Unters.*, ii. 430–444; also Poggendorff's *Ann. Jubelband*, 135 *et seq.*), that *hydrogen chloride in aqueous solution contains a hydrate*, H_2ClOH,

$$H_2ClOH = HCl + H_2O;$$

because it is precisely this hydrate-formation which is expressed by the constant 5375 c contained in the preceding formula; and this is the thermal effect due to the formation of the acid H_2ClOH from gaseous hydrogen chloride and liquid water. Now, this value is not very far removed from that of the heat of condensation of 1 gram-molecule of the gaseous substance; hence the affinity between HCl and H_2O in the hydrate is but small, confirming the high degree of dissociation of the concentrated solution.

That similar relations also hold for hydrogen bromide and hydrogen iodide is very probable, but detailed calculations were not worked out for these substances.

5. *Formic, acetic, and tartaric acids.*—Results relating to the thermal effect due to the solution in water of the two former acids are recorded in the following table, in which the numbers all refer to acids in the liquid condition :—

TABLE 8.

n	(CH_2O_2, nH_2O)	$(C_2H_4O_2, nH_2O)$
0·5	+124 c	−130 c
1	+172	−152
1·5	—	−165
2	+167	−156
4	—	−111
8	—	− 2
20	—	+173
50	+126	+278
100	+148	+335
200	+149	+375

The thermal effect with *formic acid* is in no way remarkable, but is very small. A maximum possibly occurs when n

equals 1·5, although this is by no means certain. Acetic acid on the other hand, presents some very remarkable properties.

With amounts of water varying from 0·5 to 8 molecules, *acetic acid* gives an absorption of heat, which approaches a maximum for 1·5 molecules. With 8 molecules the thermal effect is nil, but it subsequently becomes positive with larger amounts of water. That this property is connected with hydrate-formation is highly improbable; we may possibly admit the existence of a hydrate $C_2H_4O_4 . H_2O$, since the specific gravity of an acetic acid solution is a maximum for this composition, but this is entirely accidental and the result of a regular contraction on mixing acetic acid with water. The following law appears to hold:—

$$K = \frac{n \times 4{\cdot}8}{n + 1{\cdot}1} \text{ c.c.},$$

when the gram-molecule of acetic acid is put equal to 60 gr. and its molecular volume equal to 57·3 cubic centimetres. The contraction for 1 gram-molecule of $C_2H_4O_2$ then becomes

	0·5	1	2	3	4	8 grm.-mols. of water
According to the formula	1·50	2·28	3·10	3·51	3·76	4·22 c.c.
By sp. gravity	1·52	2·26	3·11	3·59	3·94	4·27 ,,

The agreement is very close; only in the case with 4 molecules of water is there a perceptible deviation, and this may almost certainly be attributed to incorrect specific gravity determination. Now, seeing that the specific gravity is a relation between the weight and the volume, the specific gravity s of a mixture $C_2H_4O_2 + nH_2O$ at about 20° C. will be

$$s = \frac{60 + 18n}{57{\cdot}3 + 18 \times 1{\cdot}0018n - \frac{4{\cdot}8n}{n + 1{\cdot}1}} = \frac{\text{weight}}{\text{volume}},$$

which is therefore a somewhat complicated function of n. On differentiating the equation, we find a maximum for n equal to 1·02—that is, for an acid with 1·02 molecules of water; this is found to be the case in practice, and can only be the result of a regular progressive contraction.

The experiments with *tartaric acid* were, of necessity, carried out with the *crystallized acid*, and the results cannot therefore be directly compared with those already described, since the other acids were investigated in the liquid condition. The results are—

$(C_4H_6O_6, nH_2O)$

$n=0$	20	50	100	200	400
−3240 c	−3307 c	−3452 c	−3516 c	−3566 c	−3600 c

The negative thermal effect is here a consequence of the passage of the solid into the liquid state; but the figures show that dilution of a solution of tartartic acid is accompanied by a feeble absorption of heat.

6. *Potassium hydroxide, sodium hydroxide, and ammonia.*—The investigations were carried out on solutions containing from 3 to 200 gram-molecules of water for each gram-molecule of KOH or NaOH, and the results are given in the following table :—

TABLE 9.

$m+3$	$(KOH.3H_2O, mH_2O)$	$(NaOH.3H_2O, mH_2O)$
5	1496 c	2131 c
7	2095	2889
9	2364	3093
20	2678	3283
25	—	3263
50	2738	3113
100	2748	3000
200	2781	2940

Thus the thermal effect is positive for both substances, and very soon attains a maximum; for the greater part of the heat developed on dissolving the anhydrous hydroxides of potassium and sodium in 200 gram-molecules of water, which

amounts respectively to 13,290 c and 9940 c, had of necessity already been evolved in the formation of the concentrated solution with 3 molecules of water, namely, 10,509 c and 7000 c respectively. If we wish to give the thermal effect starting from the anhydrous hydroxides themselves, instead of from those containing $(m + 3)$ molecules of water, we must add the last-mentioned numbers to those contained in the tables. A difference appears to exist between the heats of dilution of the potash and soda solutions, since the evolution of heat on dilution of the potash solution seems to increase with the amount of water, whilst the soda solution has a maximum value for 20 molecules of water. A solution with more than 20 molecules of water will consequently show an absorption of heat on further dilution, whilst the opposite is the case for potash solutions.

7. *Solutions of ammonia* have very small heats of dilution. It can be shown experimentally that a concentrated solution, corresponding to the formula $NH_3 + 3{\cdot}2H_2O$ develops respectively 324, 350, and 380 c on dilution with 15, 25, and 50 gram-molecules of water.

8. *Retrospect.*—It is evident from these researches that the heats of solution of the inorganic acids investigated are to a great extent dependent upon the amount of water used, and that they rise in value as this increases until, as a rule, a maximum is reached with an infinitely large amount of water. The thermal effect on dilution of aqueous solutions of acids is therefore always positive, and is a hyperbolic function, which does not suggest the formation of any hydrate other than that of the ordinary acid. In the case of the hydrogen halides the heat of absorption shows that solution in water is attended by the formation of a hydrate of the acid, corresponding, in the case of hydrogen chloride, to $ClH_2 . OH$; similar heat phenomena appear to exist for the other acids. The heats of solution of formic and acetic acids are very small, and exhibit certain peculiarities; but, nevertheless, these cannot be due to the formation of hydrates. Neither can the thermal effects for the hydroxides of potassium and sodium be explained as the result of further hydration, and we can therefore make the

general statement that *aqueous solutions of acids and alkalies contain only a single hydrate.*

B. Heats of Dilution of Solutions of Salts.

The heats of solution of salts, similarly to those of acids, are greatly influenced by the amount of water present. If the heat of solution of the anhydrous salt is negative, the negative value will increase with the amount of water, and the heat of dilution will consequently also be negative; if, on the other hand, the heat of solution is positive, this again will increase with the amount of water, and the heat of dilution of such solutions will likewise be positive. This is the general result of my researches, and only under special conditions were any exceptions observed. For example, the heat of solution of 2 gram-molecules of NH_4NO_3 is -7410 c, and falls continuously until the amount of water reaches 400 molecules, when the value is $-12{,}640$ c; whilst the heat of solution of 1 gram-molecule of $ZnCl_2$ in 5 gram-molecules of H_2O is $+7610$ c, and rises with the amount of water until, with 400 molecules, the value is $+15{,}630$ c. The heat of dilution is therefore negative for the former salt, positive for the latter. The change is in all cases a hyperbolic function of the amount of water, but it is difficult to decide upon a formula, since this would have to include at least three constants, for in addition to those already mentioned we require a value expressing the change of aggregation of a solid salt in forming a solute.

1. Numerical Results.

The following table contains the numerical results of these researches, namely, the *thermal effect due to the dilution of a salt solution* with an additional m molecules of H_2O, when it already contains n molecules of water to 1 molecule (or double molecule) of the salt, thus

$$(Q\,.\,nH_2O, mH_2O).$$

L_a gives the heat of solution of the anhydrous salt in a gram-molecules of water.

TABLE 10.

Heats of Dilution of Solutions of Salts.

Nitrates.

$n+m$	$2NaNO_3$ $n=12$	$2(NH_4)NO_3$ $n=5$	$Sr(NO_3)_2$ $n=20$	$Pb(NO_3)_2$ $n=40$
10		−1282	—	—
12	0	—	—	—
20	—	−2518	0	—
40	—	−3578	—	0
50	−2262	—	−1263	—
100	−3288	−4584	−1944	−1227
200	−3860	−5018	−2366	−1984
400	−4192	−5228	−2515	−2501
L_{400}	−10,060	−12,640	−4620	−7610

Nitrates.

$n+m$	$Mg(NO_3)_2$ $n=12$	$Mn(NO_3)_2$ $n=10$	$Zn(NO_3)_2$ $n=10$	$Cu(NO_3)_2$ $n=10$
12	0	—	—	474
15	262	934	913	744
20	412	1294	1148	940
50	404	1528	1203	904
100	364	1541	1111	776
200	370	1573	1071	729
400	421	1648	—	—

The heats of solution of these anhydrous nitrates are *positive.*

Sulphates.

$n+m$	$MgSO_4$ $n=20$	$MnSO_4$ $n=20$	$ZnSO_4$ $n=20$	$CuSO_4$ $n=60$
50	+279	+532	+318	—
100	+324	+714	+367	+ 41
200	+393	+792	+385	+116
L_{400}	+20,280	+13,790	+18,430	+15,800

	Sulphates.		Chlorides.	
$n+m$	Na_2SO_4 $n=50$	$(NH_4)_2SO_4$ $n=10$	$2NaCl$ $n=20$	$2(NH_4)Cl$ $n=20$
30	—	− 253	—	—
50	0	− 437	—	− 174
100	− 665	− 632	−1056	− 242
200	−1132	− 750	−1310	− 258
400	−1383	—	−1410	− 258
800	−1483	—	—	—
L_a	+ 460	−2370	−2360	−7760
a	400	400	200	400

Chlorides.

$n+m$	$CaCl_2$ $n=10$	$MgCl_2$ $n=10$	$ZnCl_2$ $n=5$	$NiCl_2$ $n=20$	$CuCl_2$ $n=10$
10	0	0	+ 1849	—	0
20	+ 1639	+ 2322	3152	0	+ 1630
30	—	—	—	—	2458
50	2225	3222	5317	1068	3336
100	2355	3526	6809	1380	4052
200	3515	3731	7632	1584	4510
400	—	—	8020	1697	—
L_a	+17,410	+35,920	+15,630	+19,170	+11,080
a	300	800	300	400	600

	Acetates. $Ac = 2\dot{C}_2H_3O_2$				Tartrate. $T = C_4H_4O_6$
$n+m$	K_2Ac $n=10$	Na_2Ac $n=20$	$(NH_4)_2Ac$ $n=4$	$ZnAc$ $n=50$	$(NH_4)_2T$ $n=21$
10	0	—	+1088	—	—
20	+1580	0	1800	—	—
30	—	—	—	—	− 296
50	2472	+ 664	2584	0	− 648
100	2786	832	2988	+1189	−1014
200	2998	936	3250	2248	−1242
400	3145	—	3432	3134	−1358
L_{400}	+6680	+7740	positive	positive	negative

	Bisulphates.			Carbonates.		Bicarbonate.
$n+m$	$KHSO_4$ $n=20$	$NaHSO_4$ $n=10$	$(NH_4)HSO_4$ $n=10$	K_2CO_3 $n=10$	Na_2CO_3 $n=30$	$(NH_4)HCO_3$ $n=40$
20	0	+ 436	+ 370	—	—	—
50	− 64	+ 520	+ 486	− 122	− 556	—
100	− 30	+ 558	+ 594	− 406	−1190	−176
200	+ 108	+ 702	+ 788	− 598	−1601	−288
400	+ 382	+ 972	+1048	− 749	—	−384
800	+ 766	+1193	+1366	—	—	—
L_{200}	−3800	+1190	− 20	+6490	+5640	negative

I have also investigated a solution of $2NaI + 20H_2O$, which on diluting up to 40, 100, and 200 gram-molecules of water gave a thermal effect of respectively −914, −1740, and −2058 c; whilst the heat of solution L_{200} of 2NaI amounts to +2440 c. Similarly the heats of dilution of potassium bromide and potassium cyanide are negative; the values are −10,160 c for 2KBr and −6020 c for 2KCN.

2. Theoretical Results.

(*a*) The preceding values, all the result of direct experiment, which are described in detail in *Thermochemische Untersuchungen*, vol. iii., give, therefore, the thermal effect which takes place on diluting a salt-solution of known concentration with varying proportions of water. The researches comprise 35 salts in all, and, starting from the most concentrated solution, the heat effects were measured up to a degree of dilution of from 400 to 800 gram-molecules of water for 1 gram-molecule of the salt. The choice of salt was limited to those readily soluble, since sparingly soluble salts are naturally not suited for these researches.

The most concentrated solutions contained as a rule from 10 to 20 gram-molecules of water to 1 gram-molecule of salt; but with some salts it was possible to work at a much higher concentration, thus

$NaC_2H_3O_2 + 2H_2O$, $ZnCl_2 + 5H_2O$, $NH_4NO_3 + 2{\cdot}5H_2O$.

The most important results of all these researches can be summarized as follows:—

1. Salts may be divided into two groups; in one of these the thermal effect on dilution of the aqueous solution is negative, in the other positive.
2. The heat of dilution of salt-solutions is of the same character as the heat of solution of the corresponding *anhydrous* salt on formation of very dilute solutions; if the latter be negative, the heat of dilution will likewise be negative; conversely, it is positive when the heat of solution of the anhydrous salt is positive.
3. The heat of dilution, independently of the character of the thermal effect, rises with the amount of water employed in the dilution up to a definite maximum, which as a rule is only reached at infinite dilution.
4. The positive or negative character of the heat of dilution of salt-solutions is usually dependent upon whether or not the corresponding anhydrous salt can form a crystalline hydrate; in the first case the heat of solution will be positive, as well as the heat of dilution; in the second, both will be negative (cf. p. 54).

To the *first group* belong 19 out of the 35 salts investigated, in which the *heat of dilution is positive, as is also the heat of solution* of the anhydrous salt when dissolved in a large amount of water, such as 400 to 800 gram-molecules to 1 gram-molecule of the salt, namely—

Nitrates $\begin{cases} Mg(NO_3)_2 \\ Mn(NO_3)_2 \\ Zn(NO_3)_2 \\ (CuNO_3)_2 \end{cases}$

Acetates $\begin{cases} KC_2H_3O_2 \\ NaC_2H_3O_2 \\ NH_4C_2H_3O_2 \\ Zn(C_2H_3O_2)_2 \end{cases}$

Sulphates $\begin{cases} MgSO_4 \\ MnSO_4 \\ ZnSO_4 \\ CuSO_4 \end{cases}$

Chlorides $\begin{cases} CaCl_2 \\ MgCl_2 \\ ZnCl_2 \\ NiCl_2 \\ CuCl_2 \end{cases}$

Bisulphates $\begin{cases} NaHSO_4 \\ NH_4HSO_4 \end{cases}$

To the *second group* belong the 11 following salts :—

Halides { $NaCl$, NH_4Cl, KBr, KCN }

Nitrates { $NaNO_3$, NH_4NO_3, $Sr(NO_3)_2$, $Pb(NO_3)_2$ }

Sulphate $(NH_4)_2SO_4$

Bicarbonate NH_4HCO_3

Tartrate $(NH_4)_2C_4H_4O_6$

In this group the *heats both of dilution and of solution are negative;* hence it follows that 30 out of the 35 salts investigated follow the given rule, namely, that the heat of dilution and the heat of solution of the anhydrous salt have the same character, be it positive or negative.

There remain only 5 salts which exhibit the reverse behaviour, and of which heats of dilution and of solution are of opposite sign, namely—

	Heat of dilution.	Heat of solution.
Na_2SO_4	negative	positive
NaI	,,	,,
Na_2CO_3	,,	,,
K_2CO_3	,,	,,
$KHSO_4$	positive	negative

For sodium sulphate it is noteworthy that the heat of solution is very small (in 400 and 800 gram-molecules of water it is respectively +460 and 320 c). Potassium hydrogen sulphate differs, as is shown above, from the allied sodium and ammonium salts; but that this salt must form a homogeneous solution in water follows from the fact that the difference between the heats of solution of sodium and potassium hydrogen sulphates (and consequently also the heats of dilution for the same amount of water) is a constant. The heats of solution L_a are namely—

$a=$	20	50	100	200	400	800
$NaHSO_4$	+ 924	+1008	+1046	+1190	+1460	+1681
$KHSO_4$	−3908	−3972	−3938	−3800	−3526	−3142
Difference	4832	4980	4984	4990	4986	4823

The difference between the heats of solution of these two salts in from 20 to 800 gram-molecules of water is thus a constant magnitude; which proves that the processes of solution are analogous in the two cases.

(*b*) Researches on the heats of dilution of solutions therefore show that the heat of solution of a substance is strongly influenced by the amount of water present, and approaches a maximum only at infinite dilution. The heat of solution must therefore be a hyperbolic function of the amount of water, a relation which is also observed in the researches on the heats of solution of acids.

Such a function can in many cases be approximately expressed by the simple formula

$$R_a = \frac{aC}{a + r},$$

where a represents the varying amounts of water, whilst r and C are two constants independent of the substance concerned. This formula is also applicable to the thermal effect due to the solution of acids. But with salts the relation is more complicated; for whilst the acids under investigation are liquids, the salts, on the other hand, are solids, and there must therefore be added to the formula, provided it be otherwise applicable, yet another constant corresponding to the passage of the salt in question from the solid to the liquid state. This constant must of course be negative; but in contact with water the dissolved substance may form a definite hydrate with positive heat of formation, so that whether the constant to be added to the formula be positive or negative must be determined by the special properties of the substance. The formula can thus be expressed as follows:—

$$L_a = A + \frac{aC}{a + r}.$$

If now we have experimental results for a large number of values of a, the three constants A, r, and C can be calculated, and the validity of the formula tested.

I have attempted to work out such a calculation for a few

salts. Thus the preceding investigations on the heat of dilution of ammonium nitrate gave 7 values, from which the 3 constants could be calculated. As the heat of solution L_{400} is $-12{,}640$ c, whilst the heat of dilution with from 5 to 400 gram-molecules of water, that is L_{400} to L_5, is only -5228 c, the difference between these numbers must be the heat of solution for $a = 5$, thus

$$L_5 = -12{,}640 \text{ c} + 5228 \text{ c} = -7412 \text{ c}.$$

If we now add these values to the heats of dilution contained in the tables, we obtain the heats of solution for amounts of water equal to 5, 10, 20, 40, 100, 200, and 400 gram-molecules, and the calculation leads to the following formula :—

$$L_a = -5180 \text{ c} - \frac{a}{a+12} 7640 \text{ c},$$

which gives the *heat of solution* of $2NH_4NO_3$ in *a gram-molecules of water*. The calculation for L_a gives the values found in the following table :—

a	L_a Calculated.	$L_a - L_5$ Calculated.	$L_a - L_5$ Experimental.	Difference.
5	− 7,427 c	0	0	0
10	− 8,653	−1226	−1282	−56
20	− 9,955	−2528	−2518	+10
40	−11,057	−3630	−3578	+52
100	−12,001	−4574	−4584	−10
200	−12,388	−4961	−5018	−57
400	−12,697	−5270	−5228	+42
∞	−12,820	−5393	—	—

The agreement between the experimental and calculated values is very marked; and it also shows the hyperbolic character of the heat of dilution.

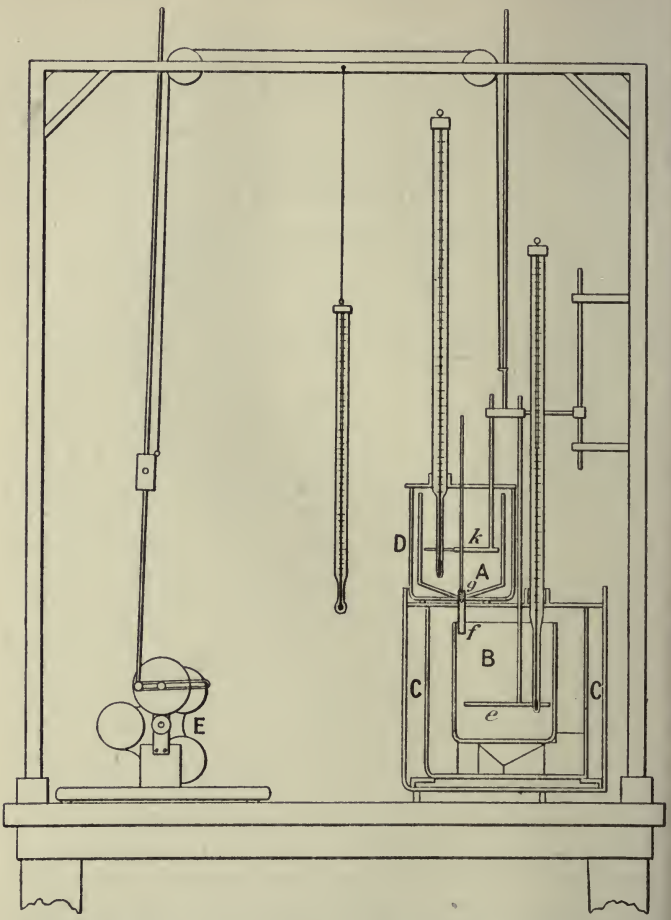
CHAPTER IV

NEUTRALIZATION OF ACIDS

A. Numerical Results.

The following chapter contains the results of my researches on the neutralization of acids. I have investigated altogether 45 acids, 31 inorganic and 14 organic, partly with the object of determining the thermal effect on formation of the normal salts, partly to ascertain how far the basicity attributed to the acids finds confirmation in the thermal effect of the reaction between acid and base. The researches described in this chapter are confined to the formation of *sodium salts*, and were carried out in aqueous solution; dilute solutions of the acids and of sodium hydroxide were mixed in varying proportions, and the resulting thermal effect was measured calorimetrically. The degrees of dilution were as a rule equal, so that the soda solution contained 200 molecules of water for each molecule of sodium hydroxide, and the acids likewise 200 molecules of water for each equivalent; dibasic acids consequently requiring 400 molecules of water per molecule of acid, and so on. As a rule the heats of reaction were determined under three conditions; namely, when acid and base were present in exactly equivalent proportions, and when there was an excess of one or other. For several acids, as, for instance, *phosphoric*, *silicic*, and *boracic*, it was necessary to extend the researches to solutions containing the reacting substances in still more varied proportions. All the experiments were carried out at a temperature of from 18° to 20° C.

In the following tables I have compared the numerical results of over 450 calorimetric experiments. The *first*, Table 11, gives the heats of neutralization of acids on formation of the



A. Platinum vessel, 500 c.c. capacity, } furnished with stirring apparatus and ther-
B. ,, ,, 1000 ,, ,, } mometers.
C. D. Outer surrounding vessels.
E. Motor for driving stirrers *k* and *e*.
f. Platinum tube connecting A and B.
g. Platinum plug closing *f*, which is withdrawn when the liquids to be mixed have acquired the same temperature.

FIG. 6.—Calorimeter for determining heats of neutralization.

normal sodium salts, and is calculated for 1 gram-molecule of acid; the *second*, Table 12, contains the results of researches dealing with the influence that an excess of either acid or sodium hydroxide has upon the heat of neutralization. For details of all these experiments the reader is referred to *Therm. Unters.*, vol. i. pp. 149–309.

TABLE 11.

Heats of Neutralization with the Formation of Normal Sodium Salts.

(*a*) *Monobasic Acids.*

Name of the acid.	*Q*	Amount of water in the acid.	(*NaOHAq*, *QAq*)
α. *Inorganic acids.*		Mol.	
1. Hydrofluoric acid .	HF	200	16,270 c
2. Hydrochloric acid .	HCl	200	13,780
3. Hydrobromic acid .	HBr	200	13,750
4. Hydriodic acid . .	HI	200	13,680
5. Hydrogen sulphide	HSH	—	7,740
6. Hypochlorous acid	HClO	400	9,980
7. Chloric acid . . .	$HClO_3$	400	13,760
8. Bromic acid . . .	$HBrO_3$	400	13,780
9. Iodic acid . . .	HIO_3	400	13,810
10. Nitric acid . . .	HNO_3	200	13,680
11. Metaphosphoric acid	HPO_3	400	14,380
12. Hypophosphorous acid . . .	HPH_2O_2	250	15,160
13. Perchloric acid . .	$HClO_4$	200	14,080
β. *Organic acids.*			
14. Hydrocyanic acid .	HCN	100	2770
15. Formic acid . . .	$HCHO_2$	200	13,450
16. Acetic acid . . .	$HC_2H_3O_2$	200	13,400
17. Propionic acid . .	$HC_3H_5O_2$	200	13,480
18. Ethylsulphuric acid	$HC_2H_5SO_4$	400	13,460
19. Monochloracetic acid . . .	$HC_2H_2ClO_2$	200	14,280
20. Dichloracetic acid .	$HC_2HCl_2O_2$	200	14,830
21. Trichloracetic acid	$HC_2Cl_3O_2$	200	13,920

(*b*) *Polybasic Acids.*

Name of the acid.	*Q*	Amount of water in the acid.	(2*NaOHAq*, *QAq*)
		Mol.	
α. Inorganic acids.			
22. Hydrosilicifluoric acid . . .	H_2SiF_6	400	26,620 c
23. Hydrogen platinichloride . .	H_2PtCl_6	600	27,220
23. Hydrogen palladochloride .	H_2PdCl_4	—	27,250
24. Sulphuric acid . .	H_2SO_4	200	31,380
25. Selenic acid . . .	H_2SeO_4	400	30,390
26. Chromic acid . .	H_2CrO_4	400	24,720
27. Sulphurous acid .	H_2SO_3	400	28,970
28. Selenious acid . .	H_2SeO_3	400	27,020
29. Dithionic acid . .	$H_2S_2O_6$	600	27,070
30. Periodic acid . .	$H_2IH_3O_6$	400	26,590
31. Arsenious acid . .	$H_2As_2O_4$	400	13,780
32. Phosphorous acid .	H_2PHO_3	400	28,450
33. Carbonic acid . .	H_2CO_3	—	20,180
34. Boracic acid . . .	$H_2B_2O_4$	300	20,010
35. Silicic acid . . .	H_2SiO_3	200	5,230
36. Stannic acid . .	H_2SnO_3	—	9,570
β. Organic acids.			
37. Oxalic acid . . .	$H_2C_2O_4$	300	28,280
38. Succinic acid . .	$H_2C_4H_4O_4$	400	24,160
39. Malic acid . . .	$H_2C_4H_4O_5$	400	26,170
40. Tartaric acid . .	$H_2C_4H_4O_6$	300	25,310
γ. Tri- and tetrabasic acids.			
41. Phosphoric acid .	H_3PO_4	450	34,030
42. Arsenic acid . . .	H_3AsO_4	200	35,920
43. Aconitic acid . .	$H_3C_6H_3O_6$	600	39,110
44. Citric acid . . .	$H_3C_6H_5O_7$	600	38,980
45. Pyrophosphoric acid	$H_4P_2O_7$	800	52,740

(*c*) *Heats of Neutralization with Formation of Barium Salts.*

In a number of cases the thermal effect on neutralization of the acids by means of a baryta solution was also measured. The result was—

Q	(BaO_2H_2Aq, Q)
H_2SO_4Aq	36,900 c
$2HClAq$	27,780
$2HBrAq$	27,780
$2HIAq$	27,780
$2HNO_3Aq$	28,260
$H_2S_2O_6Aq$	27,760
$2HClO_3Aq$	28,050
$2C_2H_5HSO_4Aq$	27,560
$2C_2H_4O_2Aq$	26,900
CO_2Aq	21,820
$2H_2SAq$	15,750
H_2SAq	7,970
$2H_3PO_2Aq$	30,930
As_2O_3Aq	14,020

TABLE 12.

Heats of Formation of Acid and Basic Sodium Salts.

No.	Q	n	$(nNaOHAq, QAq)$	m	$(NaOHAq, mQAq)$
		(*a*) *Monobasic Acids.*			
1	HF	1	16,272 c	1	16,272 c
		—	—	2	15,984
5	HSH	1	7,738	1	7,738
		2	7,802	—	—
9	HIO_3	1	13,808	1	13,808
		2	14,416	2	14,000
11	HPO_3	½	7,104	⅓	5,500
		1	14,376	½	8,192
		2	16,384	1	14,376
		3	16,500	2	14,208
12	HPH_2O_2	½	7,695	½	7,637
		1	15,160	1	15,160
		2	15,275	2	15,390
		(*b*) *Dibasic Acids.*			
24	H_2SO_4	½	7,193	¼	7,842
		1	14,754	½	15,689
		⅔	20,077	¾	15,058
		2	31,378	1	14,754
		4	31,368	2	14,386
25	H_2SeO_4	1	14,764	½	15,196
		2	30,392	1	14,764
26	H_2CrO_4	1	13,134	¼	6,291
		2	24,720	½	12,360
		4	25,164	1	13,134

No.	Q	n	$(nNaOHAq, QAq)$	m	$(NaOHAq, mQAq)$
27	H_2SO_3	1	15,870	$\frac{1}{4}$	7,332
		2	28,968	$\frac{1}{2}$	14,484
		4	29,328	1	15,870
28	H_2SeO_3	1	14,772	$\frac{1}{4}$	6,872
		2	27,024	$\frac{1}{2}$	13,512
		4	27,484	1	14,772
30	$H_2IH_3O_6$	1	5,150	$\frac{1}{5}$	6,410
		$\frac{3}{2}$	16,520	$\frac{1}{3}$	9,910
		2	26,590	$\frac{2}{3}$	11,290
		$\frac{5}{2}$	28,230	$\frac{1}{2}$	13,300
		3	29,740	$\frac{2}{3}$	11,010
		5	32,040	1	5,150
31	$H_2As_2O_4$	1	7,300	$\frac{1}{4}$	3,895
		2	13,780	$\frac{1}{3}$	5,023
		3	15,070	$\frac{1}{2}$	6,890
		4	15,580	1	7,300
32	H_2PHO_3	$\frac{1}{2}$	7,428	$\frac{1}{3}$	9,647
		1	14,832	$\frac{1}{2}$	14,244
		2	28,448	1	14,832
		3	28,940	2	14,856
33	H_2CO_3	1	11,016	$\frac{1}{4}$	5,148
		2	20,184	$\frac{1}{2}$	10,092
		4	20,592	1	11,016
34	$H_2B_2O_4$	$\frac{1}{3}$	4,524	$\frac{1}{6}$	3,440
		$\frac{1}{2}$	6,434	$\frac{1}{3}$	6,820
		1	11,101	$\frac{1}{2}$	10,005
		$\frac{6}{5}$	12,835	$\frac{2}{3}$	10,307
		$\frac{3}{2}$	15,460	$\frac{5}{6}$	10,696
		2	20,010	1	11,101
		3	20,460	2	12,869
		6	20,640	3	13,573
35	H_2SiO_3	$\frac{1}{3}$	2,652	$\frac{1}{4}$	1,353
		$\frac{1}{2}$	3,241	$\frac{1}{3}$	2,615
		$\frac{2}{3}$	3,555	$\frac{3}{4}$	3,548
		1	4,316	1	4,316
		$\frac{4}{3}$	4,731	$\frac{3}{2}$	5,332
		2	5,230	2	6,483
		4	5,412	3	7,956
37	$H_2C_2O_4$	$\frac{1}{2}$	6,904	$\frac{1}{4}$	7,125
		1	13,844	$\frac{1}{2}$	14,139
		2	28,278	1	13,844
		4	28,500	2	13,808
38	$H_2C_4H_4O_4$	1	12,400	$\frac{1}{3}$	6,096
		2	24,156	$\frac{1}{2}$	12,078
		4	24,384	1	12,400
39	$H_2C_4H_4H_5$	1	13,035	$\frac{1}{4}$	6,688
		2	26,168	$\frac{1}{2}$	13,084
		4	26,752	1	13,035
40	$H_2C_4H_4O_6$	1	12,442	$\frac{1}{3}$	8,615
		2	25,314	$\frac{1}{2}$	12,657
		3	25,845	1	12,442

No.	Q	n	(nNaOHAq, QAq)	m	(NaOHAq, mQAq)
			(c) *Tri- and Tetrabasic Acids.*		
41	H_3PO_4	½	7,329	⅙	5,880
		1	14,829	⅓	11,343
		2	27,078	½	13,539
		3	34,029	1	14,829
		6	35,280	2	14,658
42	H_3AsO_4	½	7,362	½	6,233
		1	14,994	1	11,972
		2	27,580	2	13,790
		3	35,916	3	14,994
		6	37,400	6	14,724
43	$H_3C_6H_3O_6$	1	12,848	⅙	6,683
		2	25,781	⅓	13,038
		3	39,114	½	12,890
		6	40,100	1	12,848
44	$H_3C_6H_5O_7$	1	12,672	⅙	6,954
		2	25,445	⅓	12,994
		3	38,982	½	12,722
		6	41,725	1	12,672
45	$H_4P_2O_7$	1	14,376	⅛	9,080
		2	28,644	¼	13,184
		4	52,738	½	14,322
		6	54,480	1	14,376

The numbers in this table correspond to the numbers of the acids in Table 11. The values in the fourth column show to what extent the development of heat changes when a gram-molecule of acid reacts with an increasing amount of the soda-solution, whilst the figures in the sixth column show the value of the thermal effect when a gram-molecule of sodium hydroxide reacts with varying amounts of acid.

B. Theoretical Results.

1. From the preceding numerical results of my researches on the neutralization of acids, which at first sight appear to give a motley collection of figures, we can nevertheless derive several results of a general and theoretical character, of which the following are the most important :—

(*a*) *When an aqueous solution of an acid is added to an aqueous solution containing a gram-molecule of sodium hydroxide,*

the evolution of heat is very nearly proportional to the amount of acid until the latter approaches 1, $\frac{1}{2}$, $\frac{1}{3}$, *or* $\frac{1}{4}$ *gram-molecule, according to the basicity of the acid. If, then, the amount of acid be increased beyond that required for the formation of the normal salt, only a very small additional thermal effect is observed, and this may be either positive or negative* (see Table 12, columns 5 and 6).

(*b*) *Conversely, when a soda-solution is added to an aqueous solution containing a gram-molecule of acid, the development of heat is in most cases nearly proportional to the amount of sodium hydroxide* (*often a little greater at the beginning*) *until the latter reaches* 1, 2, 3, *or* 4 *gram-molecules, according to whether the acid is mono-, di-, tri-, or tetrabasic. If the amount of soda is increased beyond these limits, no essential thermal effect is observed, provided the acid has a definite basicity and that the excess alkali does not produce a decomposition of the acid; as, for example, is the case with hydrosilicifluoric acid* (see above, Table 12, columns 3 and 4).

(*c*) It is evident from the preceding that the *basicity of an acid can be determined with certainty when the molecular weight is given, and when it has, as a whole, a definite neutralization-point.* A few examples will help to elucidate this statement.

Phosphorus forms several acids; the accepted molecular weights of four of these correspond to the formulæ H_3PO_2, H_3PO_3, H_3PO_4, and $H_4P_2O_7$. Now, when an aqueous solution containing a gram-molecule of these acids is mixed with increasing amounts of a sodium-hydroxide solution, the heat evolution is, according to Table 12—

Sodium hydroxide.	H_3PO_2	H_3PO_3	H_3PO_4	$H_4P_2O_7$
$\frac{1}{2}$ molecule . . .	7,695 c	7,428 c	7,329 c	—
1 ,, . . .	15,160	14,832	14,829	14,376
2 ,, . . .	15,275	28,448	27,078	28,644
3 ,, . . .		28,940	34,029	—
4 ,, . . .			—	52,738
6 ,, . . .			35,280	54,480

The heat of reaction therefore increases nearly proportionately to the quantity of sodium hydroxide, until the latter amounts to 1, 2, 3, and 4 gram-molecules respectively to one gram-molecule of acid, and this agrees with the accepted basicity of these acids: consequently, a further addition of soda-solution, over and above these limits, is followed by only a very small increase in the amount of heat. I have investigated a large number of acids in this manner, and the results will be found in Table 12. For many of these acids they were of special interest, and I shall now refer to them in detail.

2. *Metaphosphoric acid*, HPO_3, reacts with sodium hydroxide in aqueous solution with an evolution of 7104 c and 14,376 c respectively for $\frac{1}{2}$ and for 1 gram-molecule of the alkali; but when 2 gram-molecules of sodium hydroxide were employed an evolution of heat was obtained which varied from 16,384 c to 26,736 c in eight experiments; with 3 gram-molecules of sodium hydroxide there was produced in the first of these experiments an evolution of 16,500 c, in the last an evolution of 33,660 c.

The explanation of this peculiar behaviour is that *metaphosphoric acid in aqueous solution is in a state of continuous transformation*, so that even at 18° to 20° C., and in very dilute solution, it is fairly quickly converted into orthophosphoric acid. To prove that this is the case the following experiments were carried out. Fused and ignited metaphosphoric acid was poured into two flat platinum basins; one part immediately after cooling was examined calorimetrically; the other, which after standing for two days in a moist atmosphere had become entirely liquid through absorption of aqueous vapour, was then also dissolved in water and calorimetrically tested. The results were—

	1st experiment.	2nd experiment.
1 gram-molecule NaOHAq	= 14,376 c	14,380 c
2 ,, ,,	= 16,384	26,736
3 ,, ,,	= 16,500	33,660

A comparison with the numbers given above for orthophosphoric acid shows that after the expiration of two days metaphosphoric acid is almost entirely converted into orthophosphoric acid, that is, into a tribasic acid; whilst from the former

of these experiments we see that HPO_3 is equivalent to NaOH; that is to say, is a monobasic acid.

3. Whilst *arsenic* and *orthophosphoric acids* behave in exactly the same manner on neutralization, and give almost identical thermal effects, *arsenious acid*, on the other hand, has *entirely different properties from phosphorous acid.* Arsenic trioxide forms no known hydrate; on solution in water there is an absorption of heat, equal to -7550 c for 1 gram-molecule of As_2O_3, and on evaporation the trioxide is precipitated unchanged. Experiments prove that in *aqueous solution the molecule As_2O_3 is a dibasic acid*, with a heat of neutralization which amounts to only about one-half of that found for the other dibasic acids. According to table 12, the heats of neutralization are for

	As_2O_3Aq	$P_2O_3Aq = 2H_3PO_3Aq$
with 1 NaOHAq	7,300 c	14,856 c
,, 2 ,,	13,780	29,664
,, 4 ,,	15,070	56,896
,, 6 ,,	15,580	57,880

Thus for the same number of atoms of phosphorus and of arsenic the basicity of phosphorous acid is double that of arsenious oxide, and the heat of neutralization is almost four times as great. The composition of the solutions is therefore entirely different, and the normal sodium salts of the two acids correspond to the formulæ $Na_2As_2O_4$ and Na_2HPO_3.

4. *Hypochlorous acid* forms no characteristic salts; in aqueous solution the molecule is supposed to be monobasic and of the composition HClO. This assumption has been confirmed by experiment, which, moreover, shows that the heat of reaction is very small, amounting in the case of an acid with 800 gram-molecules of water to

1 mol. HClO and $\frac{1}{2}$ NaOHAq	5047 c
,, ,, 1 ,,	9835
,, ,, 2 ,,	9835

The molecule *HClO is therefore monobasic.* In aqueous solution the acid is not appreciably changed even after several days, nor indeed is a solution containing an excess of sodium

hydroxide; *but if there is a smaller amount of soda, so that the acid is present in excess, the latter is quickly decomposed*, and we are able to measure this change by titrating from hour to hour with stannous chloride and potassium permanganate, until after about two days all the free acid is decomposed (see *Therm. Unters.*, ii. p. 123).

5. *Hydrogen sulphide* dissolved in water behaves as a *monobasic acid* with respect to sodium hydroxide; the molecular formula is HSH, since one atom only can be replaced by sodium in aqueous solution. The heats of reaction are for

1 mol. HSHAq and 1 mol. NaOHAq 7738 c
" " 2 " " 7802

The molecule of H_2S in aqueous solution is consequently a monobasic acid similar to hydrochloric acid, but essentially different from H_2PtCl_6 and H_2SiF_6, which are dibasic acids, and in which both hydrogen atoms can be replaced by sodium. In order to prove the close similarity between aqueous solutions of hydrogen sulphide and hydrogen chloride, I have measured the heats of neutralization of these acids with respect to the soluble bases of the alkalies and alkaline earths, with the following results (see *Therm. Unters.*, iii. p. 447):—

Reaction.	$R=Mg(OH)_2$	$R=Ba(OH)_2$	$R=_2Na(OH)$	$R=_2NH_3$
(RAq, 2HClAq)	27,690 c	27,780 c	27,490 c	24,540 c
(RAq, $2H_2SAq$)	15,680	15,748	15,476	12,390
Difference	12,010	12,032	12,014	12,148

Thus we see that there is a *constant difference between the heats of reaction of HCl and of HSH with the soluble bases*, and that consequently the two acids react in a similar manner.

6. *Periodic acid.*—Whilst perchloric acid agrees in behaviour with the other monobasic acids, periodic acid shows quite characteristic neutralization phenomena. The molecular formula is generally assumed to be H_5IO_6; since the acid does not give off water on heating, unless it is at the same time decomposed, and no other hydrate is known. But the

hydrogen can be wholly, or in part, replaced by metals, and in the last case the rest of the hydrogen is, on warming, driven off as water. Salts are consequently known such as Ag_5IO_6 and $AgIO_4$, $Ag_4H_6I_2O_{12}$ and $Ag_4I_2O_9$, etc. (Rummelsberg, *Pog. Annal.*, **134**, 368 and 449). The determination of the actual basicity of the acid is therefore an interesting problem.

Owing to the sparing solubility of the sodium salt, a solution of potassium hydroxide was used in the neutralization experiments. It would appear that the maximum evolution of heat occurs when two molecules of potassium hydroxide react with each molecule of H_5IO_6. Experiments were therefore carried out with 5, 3, $\frac{5}{2}$, 2, $\frac{3}{2}$, and 1 gram-molecule of potassium hydroxide to a gram-molecule of acid. The results were as follows (see Table 12) :—

n	$(H_5IO_6Aq, nKOHAq)$	m	$(mH_5IO_6Aq, KOHAq)$
1	5,150 c	$\frac{1}{5}$	6,410 c
$\frac{3}{2}$	16,520	$\frac{1}{3}$	9,910
2	26,590	$\frac{2}{5}$	11,290
$\frac{5}{2}$	28,230	$\frac{1}{2}$	13,300
3	29,740	$\frac{2}{3}$	11,010
5	32,040	1	5,150

When n is equal to 1, a strongly *acid* liquid is formed, from which the salt very soon crystallizes out, notwithstanding that the solution contains 800 molecules of water to each molecule of salt. With n equal to $\frac{3}{2}$, the liquid is *neutral*, but from this also the salt crystallizes out; in the remaining four experiments the liquid is strongly *alkaline*.

The first table shows that the thermal effect rises rapidly with the amount of potash until this reaches 2 gram-molecules; the heat of neutralization is then equal to 26,590 c, which agrees with that of the other dibasic acids. A further addition of potash does not produce any increase in the amount of heat evolved; this has also been observed in the case of other acids. The second table shows this still more plainly. Here the heat evolution approaches a maximum when m equals $\frac{1}{2}$, just as it

did above when one molecule of acid reacted with two molecules of potassium hydroxide; but when the amount of acid is still further increased the evolution of heat is very considerably reduced. *The molecule H_5IO_6 is therefore dibasic*, and the normal potassium salt will consequently be $K_2H_3IO_6$; but this and similar salts readily give up the whole of their hydrogen as water, and it was for this reason that Rammelsberg assumed that the molecule of the acid must be regarded as double, namely—

$$2H_5IO_6 = H_4I_2O_9 . 3H_2O.$$

According to this formula, the molecule is tetrabasic, and the normal salts contain three molecules of water of crystallization.

Very remarkable is the small evolution of heat, namely 5150 c, which accompanies the formation of the acid salt when n is equal to 1; but the reason certainly is that the formation of this salt takes place according to the equation

$$H_5IO_6 + KOH = KIO_4 + 3H_2O,$$

and that consequently there is a decomposition of the acid with the separation of 3 molecules of water, which absorbs about $\frac{2}{3}$ of the normal evolution of 13,500 c, corresponding to the heat of neutralization by 1 gram-molecule of potassium hydroxide (see also *Therm Unters.*, i. p. 224, *et seq.*).

7. *Boracic acid* is known to be a very weak acid; even the theoretically acid salts, as, for instance, borax, have an alkaline reaction. Researches have shown that the *molecule B_2O_3 in aqueous solution forms a dibasic acid* with a heat of neutralization of 20,010 c, which is considerably less than that of the majority of acids; but boracic acid exhibits yet another peculiarity, as will be seen in the following table:—

n	(nNaOHAq, B_2O_3Aq)	m	(NaOHAq, mB_2O_3Aq)
$\frac{1}{2}$	6,434 c	$\frac{1}{6}$	3,440 c
1	11,101	$\frac{1}{2}$	10,005
2	20,010	1	11,101
3	20,460	2	12,869
6	20,640	3	13,573

The first table shows that the evolution of heat rises nearly proportionately to the amount of sodium hydroxide, until there are 2 molecules of NaOH to 1 molecule of B_2O_3; after this only a very small increase takes place. In the second table we see that 1 molecule of NaOH gives with boracic acid an evolution of heat which is nearly proportional to the amount of the latter, until there is a half-molecule of B_2O_3 to 1 molecule of NaOH; the molecule of the acid from B_2O_3 is therefore *dibasic*. But if we increase the amount of acid over and above the half-molecule, we find an increased evolution of heat taking place, which reaches 13,573 c for 3 gram-molecules of B_2O_3, and this is the same value that was obtained when 1 gram-molecule of NaOH neutralized 1 gram-molecule of HCl in aqueous solution; the increased amount of acid in this manner makes up for its weak character.

8. *Silicic acid* differs from all the other acids investigated, inasmuch as it does not *possess any known basicity;* moreover, the observed heat of reaction is very small, but rises equally with increased amounts of sodium hydroxide or of acid. From the numbers given in Table 12, we see that the heat of reaction of 1 gram-molecule of SiO_2 and 1 gram-molecule of NaOH is 4316 c, for 2 gram-molecules of NaOH it is 5230 c; for 1 gram-molecule of sodium hydroxide with 2 gram-molecules of silicic acid 6480 c, and so on. If now we express graphically the values found, we see that the heat of reaction is a hyperbolic function, which can be expressed approximately by the formula

$$y = \frac{xC}{x + n},$$

where y is the heat of reaction and x the number of molecules of silicic acid reacting with 1 molecule of sodium hydroxide, whilst n and C are two constants, respectively equal to 2·13 and 13,410 c. From this it would appear that the heat of reaction will rise up to 13,410 c when 1 gram-molecule of sodium hydroxide is in the presence of an infinitely large amount of silicic acid. Curiously enough, this is about the same value as was observed when boracic acid was present in sufficiently

large quantity, and this magnitude is therefore the normal heat of neutralization of 1 gram-molecule of sodium hydroxide with respect to the majority of acids.

The experiments with silicic acid were carried out both with the acid dissolved in water and also with it in the gelatinous state; but since no difference was observed in the thermal effect, we must conclude that the *change of a silicic acid solution into the gelatinous condition is not accompanied by any appreciable thermal effect.* The absence of a definite saturation point undoubtedly explains the fact that in natural silicates there are such wide limits in the ratio between base and acid.

9. The molecule of *hydrogen fluoride*, HF, has been shown to be *monobasic; its heat of neutralization is the greatest* that has been observed for any acid, namely, 16,270 c for 1 gram-molecule of sodium hydroxide; an excess of acid produces a considerable absorption of heat, which for 1 gram-molecule of acid amounts to −228 c. This property, together with the existence of acid salts of the alkali metals, and the insolubility of the fluorides of the alkaline earths, raises the question as to whether in aqueous solution the molecule of hydrogen fluoride should not be doubled.

Hydrogen fluoride not only shows a strong affinity for bases, but also *reacts vigorously with many acids*, such as boracic, silicic, stannic, and titanic acids, with which it forms compounds such as $H_2B_2F_8$, H_2SiF_6, etc. I have also measured the thermal effect of the formation of these compounds, with the following results:—

$$(B_2O_3Aq, 8HFAq) = 29{,}400 \text{ c}$$
$$(SiO_2Aq, 6HFAq) = 32{,}730$$
$$(TiO_4H_4, 6HFAq) = 30{,}900$$
$$(SnO_4H_4, 6HFAq) = 20{,}980.$$

Knowing the conditions of neutralization of these acids, I have been enabled to determine in addition that of hydrosilicifluoric acid.

10. *Hydrosilicifluoric acid is found to be dibasic;* its heat of neutralization is 26,620 c; but an excess of sodium

hydroxide produces a greatly increased evolution of heat, which for 12 gram-molecules of sodium hydroxide rises as high as 71,620 c. The explanation of this peculiar behaviour is that the *sodium silicifluoride formed is decomposed by the free sodium hydroxide* to sodium fluoride and either silicic acid or sodium silicate, according to the quantity of soda present, and this gives rise to a very large amount of heat.

11. *Monobasic acids* exhibit the simplest form of neutralization phenomena; their heats of reaction rise proportionately to the amount of sodium hydroxide, until there is one molecule of the latter to each molecule of the acid, and after this they undergo no essential change; only in the case of hydrogen fluoride, as has been already mentioned, is there any considerable absorption of heat when sodium fluoride is acted upon by hydrogen fluoride. The heats of neutralization of the majority of acids by one gram-molecule of sodium hydroxide are about equal; for 17 out of the 21 monobasic acids investigated the average value is 13,640 c; for hydrogen fluoride it is 16,270 c, the highest which has been observed; whilst for hypochlorous acid, hydrogen sulphide, and hydrogen cyanide it is very much less, being respectively 9980, 7740, and 2770 c.

The *dibasic acids*, in which two molecules of hydrogen can be replaced by sodium, can be divided into several groups, having reference to the thermal effects due to their neutralization by the first and second molecules of sodium hydroxide.

The *first* group contains the dibasic hydrogen acids *hydrogen platinichloride*, H_2PtCl_6, and *hydrosilicifluoric acid*, H_2SiF_6, in which the thermal effect is the same for the first and second molecules of sodium hydroxide.

The *second* group comprises such acids as *sulphuric*, *selenic*, *oxalic*, and *tartaric*, in which the neutralization of the first molecule of sodium hydroxide produces a smaller amount of heat than that of the second. The differences vary from 1880 to 430 c.

Sodium hydroxide.	Sulphuric acid.	Selenic acid.	Oxalic acid.	Tartaric acid.
1st molecule .	14,750 c	14,760 c	13,840 c	12,440 c
2nd molecule .	16,630	15,630	14,430	12,870
Total .	31,380 c	30,390 c	28,270 c	25,310 c

The *third* group contains *sulphurous*, *selenious*, *carbonic*, and *boracic acids*, all of which are easily converted into anhydrides. With these acids the first molecule of sodium hydroxide produces a greater thermal effect than the second; the differences lie between 1850 and 2770 c.

Sodium hydroxide.	Sulphurous acid.	Selenious acid.	Carbonic acid.	Boracic acid.
1st molecule .	15,870 c	14,770 c	11,020 c	11,100 c
2nd molecule .	13,100	12,250	9,170	8,910
Total .	28,970 c	27,020 c	20,190 c	20,010 c

When the normal sodium salts of this group are acted upon by the respective acids there is necessarily an evolution of heat, whilst with the salts of the second group there is, under the same conditions, an absorption of heat.

The *tribasic acids*, *aconitic* and *citric*, *phosphoric* and *arsenic*, also behave somewhat differently, since the heats of reaction of the first two acids are about the same for all three molecules of sodium hydroxide, although just a little greater for the third than for the first two; whilst the *heats of reaction of phosphoric acid and of arsenic acid fall off considerably for each successive molecule of sodium hydroxide.*

Sodium hydroxide.	Aconitic acid.	Citric acid.	Arsenic acid.	Orthophosphoric acid.
1st molecule .	12,850 c	12,670 c	14,990 c	14,830 c
2nd molecule .	12,930	12,770	12,590	12,250
3rd molecule .	13,330	13,540	8,340	6,950
Total .	39,110 c	38,980 c	35,920 c	34,030 c

From these values we may certainly conclude that the three hydrogen atoms replaceable by sodium in aconitic and citric acids have the same function in the molecule of the acid; and that consequently the acids are entirely tribasic in character, and have the following formulæ:—

$$C_6H_3O_3(OH)_3 \text{ and } C_6H_5O_4(OH)_3.$$

On the other hand, we must attribute to one of the three hydrogen atoms in phosphoric and arsenic acids a different function from that of the other two; and while in the first two acids mentioned we can assume the presence of three hydroxyls, in the case of the other two we must conclude that the molecule contains only two hydroxyls, and that the third hydrogen is not united to an oxygen atom. The formulæ of these acids will therefore be[1]—

$$HPO_2{}^{OH}_{OH} \qquad\qquad HAsO_2{}^{OH}_{OH},$$

which plainly indicates the difference in constitution between these two groups of tribasic acids.

The magnitude of the heat of neutralization of polybasic acids, calculated for 1 gram-molecule of NaOH, approximates to that of the monobasic acids, with the necessary exception of certain weak polybasic acids, such as carbonic, boracic, arsenious, silicic, and stannic, in which the heat of reaction is very much lower. All these researches on the neutralization phenomena of the given 45 acids show that, in spite of certain deviations, there is nevertheless a conspicuous uniformity in the results. This was certainly to be expected, since neutralization in aqueous solution consists of the mutual interaction between acid and base form to water.[2]

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[1] Note by translator.—This conclusion is modified by the hypothesis of ionization.

[2] Note by translator.—In other words, the union of $\overset{+}{H}$ and $\overset{-}{OH}$.

CHAPTER V

NEUTRALIZATION OF BASES, TOGETHER WITH SINGLE AND DOUBLE DECOMPOSITIONS

A. Methods of Investigation.

The researches now to be described follow on from those in the preceding chapter on the neutralization of acids. Their object was partly to study the heats of neutralization of 45 acids by sodium hydroxide, partly to determine the basicity of these acids.

Experiments were carried out on the heats of neutralization of 42 bases, both inorganic and organic, some soluble in water, others insoluble. The most comprehensive of the researches are those dealing with the relation of these bases to *sulphuric, nitric, and hydrochloric acids;* but other acids, such as *hydrogen sulphide*, and *carbonic, acetic, dithionic, sulphovinic acids*, etc., were also investigated. Moreover, the results convey some knowledge as to the heat phenomena concerned in single and double decomposition.

The experiments were all carried out in aqueous solutions, in which as a rule the concentration equalled 400 gram-molecules of water (7200 gr.) to one gram-molecule of a divalent base or acid, or equivalent amounts of some other acids or bases. The method of conducting these operations was more complicated than that employed in the previous chapter; this is partly due to the fact that the bases may be either soluble or insoluble in water, and partly to a desire to control the accuracy of the observations in different ways.

The experimental results contained in the next table (No. 13) were obtained in the following manner:—

(*a*) Direct measurement of the heats of neutralization of

bases. This method was employed for all the bases soluble in water, as well as for the anhydrides CuO and PbO (see Table 13 (*a*) and (*b*)).

(*b*) Precipitation of a salt-solution with sodium hydroxide (or barium hydroxide). The thermal effect is in this case the difference between the heat of neutralization of the acid by potassium hydroxide and by the base with which it was combined in the salt. This method is applicable only to insoluble bases (see Table 13 (*c*) 2).

(*c*) Precipitation of a solution of a sulphate with baryta water. The thermal effect is the difference between the heat of neutralization of sulphuric acid with the formation of barium sulphate and with the formation of the sulphate of the base under consideration. This method can be used for bases which are insoluble in water, as well as for those which are soluble; in the first case the substances contained in both solutions will be precipitated (see Table 13 (*c*) 2).

(*d*) Precipitation of a barium salt with sulphuric acid. The thermal effect is the difference between the heat of neutralization of barium hydroxide by sulphuric acid and by the acid of the salt (see Table 13 (*c*) 1).

(*e*) Exchange of metal between sulphates and barium salts; as a rule $BaCl_2$ or $Ba(NO_3)_2$ in aqueous solution. The thermal effect R is in this case the difference between two differences (equation 6, page 6); for example, for magnesium sulphate and barium chloride—

$$\left.\begin{array}{l}(BaO_2H_2Aq,\ H_2SO_4Aq) - (BaO_2H_2Aq,\ 2HClAq) \\ -(MgO_2H_2Aq,\ H_2SO_4Aq) + (MgO_2H_2Aq,\ 2HClAq)\end{array}\right\} = R.$$

From this equation one of the reactions or one of the differences can be calculated when the other magnitudes are known (see Table 13 (*f*)).

(*f*) Partial precipitation of a salt-solution with varying amounts of potassium hydroxide; by which means the heat of formation of the basic salts can be estimated.

This method is applicable to the basic salts of beryllium, ferric iron, and lead (see Table 13 (*d*)).

(*g*) Reciprocal decomposition; which serves to measure the difference between the heats of neutralization of two acids by the same base. Representing the two acids by S and S', and the equivalent amount of the base by B, we proceed to determine the thermal effect when the acid S' reacts in aqueous solution with the salt BS, and also when the acid S reacts with the salt BS'. The difference R between the thermal effects in these reactions is

$$R = (BS, S') - (BS', S) = (B, S') - (B, S),$$

which is equal to the difference between the thermal effects of the neutralization of the base by the two acids (see Table 13 (*e*)).

From amongst these various methods of estimating the heats of neutralization one or other was chosen which, according to the nature of the acid and base, seemed likely to give the most accurate results; and, when possible, this was subsequently controlled by determinations carried out in other ways. Some such examples of control experiments will now be described.

Table 13 (*a*) contains the direct heats of neutralization, estimated according to method *a*, of the soluble bases with reference to sulphuric acid. The difference between the heats of neutralization on formation of barium sulphate and of the other sulphates was also experimentally determined according to method *c* (see Table 13 (*c*) 2).

A comparison between these differences, found in two of the ways mentioned, shows the following results, in which the agreement is very satisfactory:—

R	$(BaO_2H_2Aq, H_2SO_4Aq) - (R_2O_2H_2Aq, H_2SO_4Aq)$			
		Method *a*	Method *c*	Difference
Na	36,896 c	− 31,378 c = 5518 c	5492 c	+26 c
K	36,896	− 31,288 = 5608	5632	−24
Tl	36,896	− 31,095 = 5801	5728	+73
NH_4	36,896	− 28,152 = 8744	8792	−48

Another instructive example is the determination of the differences between the heats of neutralization of sulphuric acid and of hydrochloric acid by caustic soda, potash, and ammonia, which were estimated in three different ways: partly by the direct method, partly by noting the thermal effect on decomposition of the sulphates by $BaCl_2$, and finally by the reciprocal decomposition method. Since the difference between the heats of neutralization of barium sulphate and of barium chloride, according to direct experiments (Table 13 (*a*)), amounts to 9112 c, and the thermal effect on double decomposition of the sulphates of sodium, potassium, and ammonium with barium chloride (according to Table 13 (*f*)) amounts respectively to 5240, 5280, and 5408 c, so the difference between 9112 c and these numbers will give the differences between the heats of neutralization of sulphuric acid and of hydrochloric acid with respect to these three bases—that is, 3872, 3832, and 3704 c. The same values can also be derived from the reciprocal decomposition results (Table 13 (*e*)), and finally by direct measurements of the heats of neutralization (Table 13 (*a*)). We thus obtain the following three values for this difference, namely :—

Method		Sodium hydroxide	Potassium hydroxide	Ammonia
a	Direct determination . . .	3890 c	3784 c	3608 c
e	Double decomposition . . .	3872	3832	3704
g	Reciprocal decomposition . .	3852	3808	3608
	Mean value . .	3871 c	3808 c	3673 c

Thus the three methods give identical results, which is a guarantee both of their suitability and of the accuracy of the experiments.

All details concerning this research, which comprises over 300 calorimetrical experiments, will be found in *Therm. Unters.*, i. pp. 310 to 449. The subject-matter is arranged as follows :—

(*a*) *Alkalies and alkaline earths :* The hydroxides of lithium, sodium, potassium, ammonium, barium, strontium, and calcium, as well as thallous hydroxide.

(*b*) *Magnesia group:* Magnesium, manganous, nickelous, cobaltous, ferrous, cadmium, zinc, and copper hydroxides.

(*c*) *Hydrated sesquioxides* of beryllium,[1] aluminium, chromium, and ferric iron.

(*d*) *Hydrated oxides* of the rare earths: Hydroxides of lanthanum, cerium, didymium, yttrium, and erbium.

(*e*) *Anhydrous oxides:* Lead oxide, mercurous and mercuric oxides, and also silver oxide.

(*f*) *Organic bases:* Ethylamine, methyl-, dimethyl-, and trimethylamine, tetramethylammonium hydroxide, triethylsulphonium hydroxide, platinodiammonium hydroxide, aniline, toluidine, hydroxylamine, methylquinine hydroxide, triethylstibine oxide, and urea.

In Table 13 are given first the results of direct experiments, arranged according to the methods employed; and subsequently, in Table 14, the experimental heats of neutralization of all these bases, arranged in groups with respect to the several acids investigated.

B. Numerical Results.

TABLE 13.

Direct Experimental Results.

(*a*) *Neutralization of Soluble Inorganic Bases.*

B	(*BAq*, H_2SO_4Aq)	(*BAq*, 2*HClAq*)	(*BAq*, $2HNO_3Aq$)
2LiOH	31,288 c	27,696 c	—
2NaOH	31,378	27,488	27,364 c
2KOH	31,288	27,504	27,544
2TlOH	31,095	47,680[2]	27,380
$Ba(OH)_2$	36,896[2]	27,784	28,264
$Sr(OH)_2$	30,710	27,630	—
$Ca(OH)_2$	31,140	27,900	—
$2NH_3$	28,152	24,544	24,644

[1] See note on p. 130.

[2] Valid when $BaSO_4$ and Tl_2Cl_2 are precipitated.

To these we may add the heat of neutralization of ammonia with acetic acid, and that of certain oxides—

$$2(NH_3Aq,\ C_2H_4O_2Aq) = 24{,}020 \text{ c}$$
$$(CuO,\ H_2SO_4Aq) = 18{,}130$$
$$(PbO,\ 2HNO_3Aq) = 17{,}775$$
$$(PbO,\ 2C_2H_4O_2Aq) = 15{,}468$$

In all these processes the salt formed remains in solution.

(*b*) *Neutralization of Organic Bases.*

Base	*B*	$(BAq,\ H_2SO_4Aq)$	$(BAq,\ 2HClAq)$
Ethylamine	$2C_2H_5NH_2$	—	26,880 c
Methylamine . . .	$2CH_3NH_2$	—	26,230
Dimethylamine . . .	$2(CH_3)_2NH$	—	23,620
Trimethylamine . . .	$2(CH_3)_3N$	21,080 c	17,480
Tetramethylammonium hydroxide	$2(CH_3)_4NOH$	31,032	27,490
Triethylsulphonium hydroxide	$2(C_2H_5)_3SOH$	30,590	27,440
Platinodiammonium hydroxide	$(NH_3)_4PtO_2H_2$	30,850	27,300
Hydroxylamine . . .	$2NH_3O$	—	18,520
Methylquinine hydroxide	$2C_{21}H_{27}N_2O_2OH$	—	21,680
Triethylstibine oxide .	$Sb(C_2H_5)_3O$	3,650	—

(*c*) *Single Decompositions.*

1. Sulphuric Acid and Salts of Barium or Lead.

Q	$(QAq,\ H_2SO_4Aq)$
$BaCl_2$	9152 c
$Ba(NO_3)_2$	8560
BaS_2O_6	9136
$Ba(ClO_3)_2$	8840
$Ba(H_2PO_2)_2$	5965
$Ba(C_2H_5SO_4)_2$	9336
$Ba(C_2H_3O_2)_2$	9992
$Pb(NO_3)_2$	5448
$Pb(C_2H_3O_2)_2$	7656

2. Sulphates and the Hydroxides of Barium or Potassium.

Q	(QAq, BaO_2H_2Aq)	$(QAq, 2KOHAq)$
Na_2SO_4	5,492 c	—
K_2SO_4	5,632	—
Tl_2SO_4	5,728	—
$(NH_4)_2SO_4$	8,792	—
$MgSO_4$	5,840	−88 c
$MnSO_4$	10,304	+4,912
$NiSO_4$	10,628	5,532
$CoSO_4$	12,224	5,888
$FeSO_4$	12,004	6,340
$CdSO_4$	13,072	7,066
$ZnSO_4$	13,428	7,936
$CuSO_4$	18,456	12,376
Ag_2SO_4	—	16,800
$\frac{1}{3}Fe_2(SO_4)_3$	—	19,984
$BeSO_4$	—	15,192
$\frac{1}{3}La_2(SO_4)_3$	9,458	—
$\frac{1}{3}Ce_2(SO_4)_3$	10,872	—
$\frac{1}{3}Di_2(SO_4)_3$	11,175	—
$\frac{1}{3}Y_2(SO_4)_3$	11,826	—
$\frac{1}{3}Al_2K_2(SO_4)_4$	16,000	10,176
$\frac{1}{3}Cr_2K_2(SO_4)_4$	—	14,848
$\frac{1}{3}Fe_2K_2(SO_4)_4$	—	20,040
$(NH_3O)_2H_2SO_4$	15,320	—
$(NC_6H_7)_2H_2SO_4$	—	12,900

To this group we may add—

$$(Cu\,.\,2C_2H_3O_2Aq,\ BaO_2H_2Aq) = 14{,}072\text{ c}$$
$$(Er_2\,.\,6C_2H_3O_2Aq,\ 3BaO_2H_2Aq) = 25{,}680$$
$$(2AgNO_3Aq;\ BaO_2H_2Aq) = 17{,}380$$
$$(CO_2\,.\,N_2H_6\,.\,150H_2O,\ BaO_2H_2Aq) = 4{,}971$$
$$(CO_2\,.\,N_2H_6\,.\,400H_2O,\ BaO_2H_2Aq) = 5{,}920$$

(*d*) *Partial Decompositions.*

n	$(3BeSO_4Aq, nKOHAq)$	$(Fe_2Cl_6Aq, nNaOHAq)$
2	18,900 c	17,040 c
3	26,784	25,308
4	33,426	33,408
6	45,576	49,008

n	$(PbN_2O_6Aq, nNaOHAq)$	$(PbC_4H_6O_4Aq, nKOHAq)$
½	6,396 c	4,332 c
1	12,678	8,196
2	11,952	—
4	11,064	—
12	8,260	—

We may also add—

$$(PbO.PbC_4H_6O_4Aq, 2HNO_3Aq) = 12{,}037 \text{ c}$$

(*e*) *Reciprocal Decompositions.*

V	A (VCl_2Aq, H_2SO_4Aq)	B $(VSO_4Aq, 2HClAq)$	$A-B$
Na_2	+488 c	−3364 c	3852 c
K_2	620	−3188	3808
$(NH_4)_2$	628	−2960	3588
Mg	930	−2592	3522
Mn	1056	−2528	3584
Fe	1096	−2492	3588
Zn	1124	−2464	3588
Co	1152	−2436	3588
Ni	1132	−2382	3514
Cu	1252	−2292	3544

To these we may add—

$$(K_2SO_4Aq, 2HNO_3Aq) = -2968 \text{ c}$$
$$(2KNO_3Aq, H_2SO_4Aq) = +\ 709$$

(*f*) *Double Decompositions.*

1. Sulphates and Barium Salts.

Q	$(QAq, BaCl_2Aq)$	(QAq, BaN_2O_6Aq)
Na_2SO_4	5240 c	4680 c
K_2SO_4	5280	—
$(NH_4)_2SO_4$	5408	5048
$MgSO_4$	5600	4936
$MnSO_4$	5600	—
$CoSO_4$	5688	—
$CdSO_4$	5683	5128
$ZnSO_4$	5504	—
$CuSO_4$	5616	5080

Q	$(QAq, 3BaCl_2Aq)$	Q	$(QAq, 4BaCl_2Aq)$
$3BeSO_4$	19,980 c		
$Fe_2(SO_4)_3$	27,432		
$La_2(SO_4)_3$	20,016	$K_2Al_2(SO_4)_4$	25,628 c
$Ce_2(SO_4)_3$	21,762	$K_2Cr_2(SO_4)_4$	24,544
$Di_2(SO_4)_3$	22,140		
$Y_2(SO_4)_3$	22,842		

Q	$(QAq, BaC_4H_6O_4Aq)$	$(QAq, BaC_4H_{10}S_2O_8Aq)$
Na_2SO_4	5040 c	4884 c
K_2SO_4	5136	—
$CaSO_4$	—	5784
$ZnSO_4$	4608	—
$CuSO_4$	4368	5736
$\frac{1}{3}Fe_2(SO_4)_3$	6736	—

To these we may add—

$$(MgSO_4Aq,\ BaS_2O_6Aq) = 5456 \text{ c}$$
$$(CdSO_4Aq,\ BaS_2O_6Aq) = 5600$$
$$\tfrac{1}{3}(Fe_2(SO_4)_3Aq,\ BaN_2O_6Aq) = 8592$$
$$(Na_2SO_4Aq,\ BaCl_2O_6Aq) = 4980$$
$$(CuSO_4Aq,\ BaCl_2O_6Aq) = 5950$$
$$\tfrac{1}{3}(Fe_2(SO_4)_3Aq,\ BaCl_2O_6Aq) = 9340$$

2. Salts of Lead, Strontium, and Calcium.

$$(PbN_2O_6Aq,\ Na_2SO_4Aq) = \ 1712 \text{ c}$$
$$(SrCl_2Aq,\ Na_2SO_4Aq) = -300$$
$$(CaCl_2Aq,\ Na_2SO_4Aq = -438$$

We have here data by means of which the heats of neutralization of the bases, and the values derived from them, can be calculated. The results of these calculations are arranged in systematic order in the following tables :—

TABLE 14.

Heats of Neutralization of Bases.

(a) Sulphuric Acid, Hydrochloric Acid, and Nitric Acid.

1. Inorganic Bases.

Q	Sulphuric acid (Q, H_2SO_4Aq)	Hydrochloric acid (Q, $2HClAq$)	Nitric acid (Q, $2HNO_3Aq$)
$2KOHAq$	31,290 c	27,500 c	27,540 c
$2NaOHAq$	31,380	27,490	27,360
$2LiOHAq$	31,290	27,700	—
$2TlOHAq$	31,130	27,480	27,380
$Ba(OH)_2Aq$	36,900 *	27,780	28,260
$Sr(OH)_2Aq$	30,710	27,630	—
$Ca(OH)_2Aq$	31,140	27,900	—
$Mg(OH)_2$	31,220	27,690	27,520
$Mn(OH)_2$	26,480	22,950	—
$Ni(OH)_2$	26,110	22,580	—
$Co(OH)_2$	24,670	21,140	—
$Fe(OH)_2$	24,920	21,390	—
$Cd(OH)_2$	24,220	20,290	20,620
$Zn(OH)_2$	23,410	19,880	19,830
$Cu(OH)_2$	18,440	14,910	14,890
CuO	18,800	15,270	15,250
PbO	23,380 *	15,390	17,770
HgO	—	18,920	6,400
Hg_2O	—	30,070 *	5,790
Ag_2O	14,490	42,380 *	10,880
$2NH_3Aq$	28,150	24,540	24,640

The values marked with an asterisk are valid for neutralization when there is complete precipitation of the compound formed; in all the other examples the salt remains in solution. For *thallium*, the thermal effect with formation of the insoluble chloride is 47,680 c. Hydrobromic and hydriodic acids behave, as a rule, in the same way as hydrochloric acid, provided the resulting compounds are soluble. The evolution of heat on neutralization of these three acids by means of the hydroxides of sodium, barium, zinc, magnesium, and copper is the same; but this is not the case for cadmium hydroxide (see p. 130).

Q	Sulphuric acid (Q, $3H_2SO_4Aq$)	Hydrochloric acid (Q, $6HClAq$)
$La_2O_3 . xH_2O$	3 × 27,470 c	3 × 25,020 c
$Ce_2O_3 . xH_2O$	3 × 26,030	3 × 24,160
$Di_2O_3 . xH_2O$	3 × 25,720	3 × 23,980
$Y_2O_3 . xH_2O$	3 × 25,070	3 × 23,570
$Al_2O_3 . xH_2O$	3 × 20,990	3 × 18,640
[1] $Be_3O_3 . xH_2O$	3 × 16,100	3 × 13,640
$Cr_2O_3 . xH_2O$	3 × 16,440	3 × 13,730
$Fe_2O_3 . xH_2O$	3 × 11,280	3 × 11,150

2. ORGANIC BASES.

Q	Sulphuric acid (QAq, H_2SO_4Aq)	Hydrochloric acid (QAq, $2HClAq$)
1 mol. Platinodiammonium hydroxide	30,850 c	27,300 c
2 ,, Triethylsulphonium hydroxide	30,590	27,440
2 ,, Tetramethylammonium hydroxide.	31,030	27,490
2 ,, Ammonia	28,150	24,540
2 ,, Methylamine	—	26,230
2 ,, Dimethylamine	—	23,620
2 ,, Trimethylamine	21,080	17,480
2 ,, Ethylamine	—	26,880
2 ,, Hydroxylamine	21,580	18,520
2 ,, Methylquinine hydroxide	—	21,680
1 ,, Triethylstibine oxide	3,650	—
2 ,, Aniline	18,480	(15,480)*
2 ,, Toluidine	(18,540)*	15,240

The values marked with an asterisk are calculated from the heats of neutralization found experimentally for the other acids; 2 gram-molecules of hydroxylamine with 2 gram-molecules of HNO_3 give a heat of neutralization of 18,840 c.

[1] See footnote, p. 130.

(*b*) *Carbonic Acid, Hydrogen Sulphide, and Acetic Acid.*

Q	Carbonic acid (Q, CO_2Aq)	Hydrogen sulphide (Q, $2HSHAq$)	Acetic acid (Q, $2C_2H_4O_2Aq$)
$2NaOHAq$	20,180 c	15,480 c	26,790 c
$2KOHAq$	—	—	26,430
$Ba(OH)_2Aq$	21,820	15,750	26,900
$Sr(OH)_2Aq$	20,550	—	—
$Ca(OH)_2Aq$	18,310	—	—
$Mg(OH)_2$	—	15,680	26,400
$2NH_3Aq$	16,850[1]	12,390	24,020

Q	Carbonic acid (Q, CO_2Aq)	Hydrogen sulphide (Q, SH_2Aq)	Acetic acid (Q, $2C_2H_4O_2Aq$)
$Mn(OH)_2$	13,230 c	10,700 c	—
$Ni(OH)_2$	—	18,630	—
$Co(OH)_2$	—	17,410	—
$Fe(OH)_2$	—	14,570	—
$Cd(OH)_2$	12,990	27,370	—
$Zn(OH)_2$	—	17,970	18,030 c
$Cu(OH)_2$	—	—	12,820
CuO	—	31,670	13,180
PbO	16,700	29,200	15,470
HgO	—	45,300	—
Tl_2O	—	38,490	—
Cu_2O	—	38,530	—
Ag_2O	14,180	58,510	—
$Fe_2O_3 . 3H_2O$	—	—	$3 \times$ 8,020
$Er_2O_3 . xH_2O$	—	—	$3 \times$ 18,340

For gaseous carbon dioxide the thermal effect is 5880 c greater.

[1] This number applies to the formation of $CO_2 . 2NH_3$ when the amount of water present is 150 gram-molecules; with 400 gram-molecules of water the thermal value is 15,900 c.

(*c*) *Dithionic Acid, Ethylsulphuric Acid, and Chloric Acid.*

(*Q*, *RAq*)

Q	*R*		
	$H_2S_2O_6$	$2(C_2H_5HSO_4)$	$2(HClO_3)$
2NaOHAq	27,070 c	26,930 c	27,520 c
$Ba(OH)_2Aq$	27,760	27,560	28,050
$Mg(OH)_2$	27,540	—	—
$Co(OH)_2$	—	21,120	—
$Cd(OH)_2$	20,360	—	—
$Cu(OH)_2$	—	14,840	15,550
$\frac{1}{3}Fe_2(OH)_6$	—	—	10,780

(*d*) *Phosphorous Acid and Arsenious Acid.*

(*Q*, *RAq*)

Q	$R = 2H_3PO_2$	$R = As_2O_3$
2NaOHAq	30,320 c	13,780 c
$Ba(OH)_2Aq$	30,930	14,020

These tables contain the values for the heats of neutralization of eleven acids with different bases (41 in all), to which may be added the values given in a previous chapter for the heats of neutralization, with formation of sodium salts, of 45 acids. In a later chapter the results of researches on the thermal properties of hydrobromic and hydriodic acids will be described, and it will be shown that these acids agree very closely in properties with hydrochloric acid.

C. General Character of the Phenomena of Neutralization.

1. *Inorganic and organic bases soluble in water.*—From a general chemical standpoint neutralization is regarded as a

union of acid hydrogen and basic hydroxyl to form water. It is therefore also probable that the heat phenomena accompanying neutralization will, under similar conditions, have a common character. Furthermore, it is an obvious conclusion that these phenomena must occur in their simplest form when the acids and bases compared in each group are of similar constitution, and when both acid and base, as well as the salt formed, are soluble in water and the reaction is carried out in dilute aqueous solutions. This assumption is confirmed by experiment.

Amongst the inorganic bases soluble in water are the two main groups of the *alkalies* and *alkaline earths*, which form either mono- or divalent bases in which the molecules are supposed to correspond to the formulæ ROH or $R(OH)_2$. With these are associated a series of organic bases of similar constitution; that is to say, containing basic hydroxyl groups, such as the *quaternary ammonium bases* and *triethylsulphonium hydroxide*, as well as *platinodiammonium hydroxide* and analogous substances.

Researches have shown that *for the same acid all these substances have equal heats of neutralization*, and that consequently the difference between the heats of neutralization of two acids for any given base is always the same. Moreover, it has been found that the heats of neutralization of a very large number of acids are of equal value, such as hydrochloric, hydrobromic, and hydriodic acids; nitric acid, chloric, bromic, and iodic acids; formic, acetic, and propionic acids; also ethylsulphuric acid; and among the polybasic acids hydrosilicifluoric acid, hydroplatinichloric acid, dithionic acid, etc. It therefore follows that for the majority of bases soluble in water the neutralization is accompanied by an approximately equal thermal effect.

The following summary shows the equality of the *heats of neutralization of the soluble bases corresponding to the formula* $R(OH)_n$ with sulphuric acid and hydrochloric acid:—

Name of the base.	Sulphuric acid.	Hydrochloric acid.	Difference.
Lithium hydroxide	31,290 c	27,700 c	3590 c
Sodium hydroxide	31,380	27,490	3890
Potassium hydroxide	31,290	27,500	3790
Thallous hydroxide	31,130	27,480	3650
Barium hydroxide	(31,280)	27,780	3530
Strontium hydroxide	30,710	27,630	3080
Calcium hydroxide	31,140	27,900	3240
Magnesium hydroxide	31,220	27,690	3530
Platinodiammonium hydroxide	30,850	27,300	3550
Triethylsulphonium hydroxide	30,590	27,440	3150
Tetramethylammonium hydroxide	31,030	27,490	3540
Mean value	31,090 c	27,590 c	3500 c

All values are calculated for two gram-equivalents of the base—that is, for $Ba(OH)_2$ or $2KOH$, etc.; furthermore, the last column contains the differences between the thermal effects for the two acids.

The value for the formation of barium sulphate is calculated according to the method given on p. 137; provided the salt is precipitated, the heat of reaction rises to 36,900 c.

From the preceding table it is evident that the neutralization of each of the bases referred to by the same acid produces an equal thermal effect, and that consequently there is a constant difference between the heats of neutralization of two acids by the same base. The value found for the neutralization of hydrochloric acid, namely 27,590 c, is the same as that which is found for the greater number of the above-mentioned acids; but the investigation of all the bases named has not been carried out. The following table gives some of these numbers:—

Base.	Nitric acid.	Dithionic acid.	Chloric acid.	Ethyl-sulphuric acid.	Acetic acid.	Hydrogen sulphide $2HSH$
$2KOHAq$	27,540 c	—	—	—	26,430 c	—
$2NaOHAq$	27,360	27,070 c	27,520 c	26,930 c	26,790	15,480 c
$2TlOHAq$	27,380	—	—	—	—	—
$Ba(OH)_2$	28,260	27,760	28,050	27,500	26,900	15,750
$Mg(OH)_2$	27,520	27,540	—	—	26,400	15,680
Mean value	27,610 c	27,460	27,780 c	27,220 c	26,630 c	15,640 c

For the first four of these acids the mean value is 27,520 c, which is in complete agreement with the figure found for hydrochloric acid; for acetic acid it is just a little lower, while again the same value is given by formic and propionic acids. *Hydrogen sulphide* is also to be found in the table, although it belongs to a group of acids with far lower heats of neutralization; yet, nevertheless, also for this acid the lower values of the heats of neutralization are equal for each of the bases investigated. Furthermore, it is evident from the figures contained in the tables that *thallous hydroxide* behaves similarly to the hydroxides of the alkali metals, which was only to be expected from its solubility in water and general chemical properties, and that *magnesium hydroxide* has the same thermal properties as the hydroxides of the alkaline earths, while, as will be demonstrated later on, it is also intermediate in properties between the other bases and those of the so-called magnesium group with respect to its heat of neutralization; it is certainly not soluble in water, and its heat of solution is exceedingly small, possibly zero (see below). On the other hand, *magnesium hydrosulphide dissolves in water* to the same extent as the corresponding compounds of barium, strontium, and calcium, and the heat of neutralization is the same for these four bases; and this also applies to hydrogen sulphide. Lead monoxide, however, differs completely from the alkaline earths, not only in its heat of neutralization, but also in other chemical and physical properties; it is solely due to the isomorphism of certain salts of lead and of the alkaline earths that lead has sometimes been placed among the last-mentioned group of elements.

2. *The soluble bases of the ammonia group* show much greater differences on neutralization than the bases referred to above which contain basic hydroxyl groups. An aqueous solution of ammonia or of an amine is as poor in hydroxyl ions as a solution of carbonic acid is in hydrogen ions, and the reaction with acids will therefore be entirely different from that of the bases already described.

Methylquinine hydroxide is possibly a quaternary base similar to tetramethylammonium hydroxide, and we might

therefore expect that it would have an equal heat of neutralization. Experiments, however, show that the value is less by 5810 c, and this is due to the fact that the basic radical contains oxygen, which decreases its basic character. The same is observed on comparing the heats of neutralization of the aliphatic and aromatic amines; for whilst the values for methylamine and for ethylamine are equal (namely 26,560 c), as are also those for aniline and toluidine (15,360 c), there is nevertheless a difference of 11,200 c between the first and last mentioned numbers. This fact is explained by the different characters of the corresponding radicals, since C_6H_5, unlike the neutral alkyl radicals CH_3 and C_2H_5, is of a weakly acid nature, which is apparent both in the distinctly acid hydroxyl compound C_6H_5OH, and also in the amido-compound $C_6H_5NH_2$, which scarcely reacts alkaline in aqueous solution. The small thermal effect due to the reaction between the aromatic amines and an acid is also a result of the weakly basic character of the radical. For the same reason *hydroxylamine* (NH_2OH) has a lower heat of reaction than ammonia; the difference amounts to 6020 c.

The heats of neutralization of 2 gram-molecules of the bases of the ammonium group which have been investigated are compared in the following tables:—

Base.	Formula.	Heat of neutralization.	
		Sulphuric acid.	Hydrochloric acid.
Ammonia	$2NH_3$	28,250 c	24,540 c
Ethylamine	$2C_2H_5NH_2$	—	26,880
Methylamine	$2CH_3NH_2$	—	26,230
Dimethylamine	$2(CH_3)_2NH$	—	23,620
Trimethylamine	$2(CH_3)_3N$	21,080	17,480
Hydroxylamine	$2NH_3O$	21,580	18,520
Aniline	$2C_6H_5NH_2$	18,480	(15,480)
Toluidine	$2C_7H_7NH_2$	(18,540)	15,240
Methylquinine hydroxide	$2C_{21}H_{27}N_2O_2OH$	—	21,680

A comparison between ammonia and the *aliphatic amines* shows that whilst the primary amines have a greater heat of neutralization than ammonia, the secondary amines have a lower value, while that of the tertiary amines is still smaller. The numbers are respectively 26,230, 23,620, and 17,480 c.

All the soluble bases referred to are seen to have lower heats of neutralization than the soluble bases of the formula $R(OH)_n$; but here again we observe, as before, a difference of 3500 c between the heats of neutralization of sulphuric acid and hydrochloric acid.

It should also be mentioned that 2 gram-molecules of *triethylstibine oxide* react in aqueous solution with 1 gram-molecule of sulphuric acid to give only 3650 c, which consequently proves that this substance is very weakly basic in character. Also, when 2 gram-molecules of *urea* react in aqueous solution with nitric acid the thermal effect is only 330 c, thus showing that the basic character is very little removed from zero, owing to the presence of the carbonyl radical in $CO(NH_2)_2$.

3. To the *magnesia group* of the general formula $R(OH)_2$ belong the corresponding compounds of Mg, Mn, Ni, Co, Fe, Zn, and Cu; sometimes $Cd(OH)_2$ is included in this group, but this is incorrect, as will be demonstrated later. The heats of neutralization are determined by noting the thermal effect when an aqueous solution of a soluble sulphate is precipitated by means of potassium or barium hydroxide; two series of reactions were carried out, and the mean values taken. The heats of neutralization of the other acids are determined from the thermal effect on double decomposition of the sulphates with the barium salt of the acid in question. In the case of hydrochloric acid the results were further controlled by the reciprocal decomposition method, by means of which the difference between the heats of neutralization of sulphuric acid and of hydrochloric acid is determined (see table 13 (ϵ)). Here again, as in the case of the soluble bases referred to above, the two methods give conformable results with respect to the difference between the heats of neutralization of the two acids

$$(MO_2H_2,\ H_2SO_4Aq) - (MO_2H_2,\ 2HClAq).$$

The values found are recorded in the next table.

M	Reciprocal decomposition.	Double decomposition.	$(MO_2H_2, 2HClAq)$
Mg	3522 c	3512 c	27,690 c
Mn	3584	3512	22,950
Ni	3514	—	22,580
Co	3588	3424	21,140
Fe	3588	—	21,390
Zn	3588	3608	19,880
Cu	3544	3496	14,910
Mean value	3560 c	3510 c	

The difference in the heats of neutralization can therefore be placed at 3530 c, and from this value and the heat of neutralization of sulphuric acid the corresponding difference for hydrochloric acid can be found. The group of soluble bases gave 3500 c for this difference (see p. 125). It is evident from the numbers in the tables that the heats of neutralization of the bases of the magnesia group are equal to those of the soluble bases with respect to hydrochloric, dithionic, ethylsulphuric, nitric, and chloric acids.

Whilst the heats of neutralization were found to be equal for all the soluble hydroxyl-bases, in spite of the fact that the atomic weights of the metals concerned varied from 7 for lithium to 204 for thallium, the values for the magnesia series are very unequal, in some cases the numbers for the heats of neutralization fall off with an increase of atomic weight. For magnesium hydroxide, which behaves like the alkaline earths, the value amounts to 27,690 c, for manganous hydroxide it has already fallen to 22,950 c, and for copper hydroxide it is only 14,910 c.

4. The neutralization phenomena of *cadmium hydroxide* have been thoroughly investigated, since they present essential differences from those of the magnesia group (see *Therm Unters.*, iii. 279, *et seq.*). Researches which have been carried out with the hydroxides of magnesium, zinc, and copper, show that with aqueous solutions of hydrochloric, hydrobromic, and

hydriodic acids, each of these bases gives precisely the same heat of neutralization, which is only what the neutralization experiments with sodium hydroxide and these acids would lead us to expect; but cadmium hydroxide behaves quite differently, since its heat of neutralization rises appreciably as we proceed from hydrochloric to hydrobromic and hydriodic acids. The values found are—

	$Zn(OH)_2$	$Mg(OH)_2$	$Cu(OH)_2$	$Cd(OH)_2$
2HClAq[1]	19,483 c	27,313 c	14,602 c	20,295 c
2HBrAq	19,647	—	14,748	21,561
2HIAq	19,606	27,312	—	24,208

This marked increase in the heat of neutralization is exceptional, none of the bases hitherto described exhibited such a property; but we shall find somewhat similar behaviour when we come to the oxides of lead and mercury, so that undoubtedly cadmium hydroxide should not be classed in the magnesia group, with which its compounds[2] present only few slight resemblances.

5. *Sesquioxides of La, Ce, Di, Y, Al, Be,*[3] *Cr, and Fe.*—The

[1] The deviation of from 300 to 400 c between these values for hydrochloric and those given in table 14 (*a*) 1 are due to differences in the degree of dilution.

[2] Footnote by translator.—Cadmium salts are notably less ionized than those of the other metals mentioned, when compared under equal molecular dilutions.

[3] Footnote by translator.—It is now known that the atomic weight of beryllium is 9·1 and not 13·65; that it is a dyad and not a triad as it was supposed to be when Thomsen's measurements were made. Nevertheless, since the thermal properties of beryllium hydroxide are precisely similar to those of the hydroxides of aluminium and chromium, and inasmuch as the heats of reaction are not proportional to the amount of acid (see p. 131), and the heat of neutralization of BeO, H_2O is exactly the same as that of Al_2O_3, H_2O and Cr_2O_3, H_2O, whilst it is only half of that of the equivalent amount of magnesium hydroxide, beryllium has been left in the tables with the sesquioxides, and the molecular formula of its oxide is there, for purpose of comparison, represented as Be_3O_3.

results of investigation of these bases, which are given on p. 121, show that the rare earths, lanthanum oxide in particular, must be classed with the strong bases; the highest heat of neutralization approaches very nearly to that of magnesium hydroxide, but the value falls off continuously until for the hydroxides of aluminium and beryllium it is only a half. But, here again, we observe that the heat of neutralization is greater for sulphuric than for hydrochloric acid; the difference is, however, less than for the bases previously mentioned.

Ferric hydroxide exhibits a peculiar property, since the heat of neutralization is the same for sulphuric, hydrochloric, nitric, and chloric acids (11,200 c for each gram-molecule of sulphuric acid); but for acetic acid the value falls to 8020 c.

It is probable that with all these bases the first molecule of acid gives a greater heat effect than the second, and that the third gives less than the second. Further experiments were made with beryllium hydroxide, and the values found for 3 gram-molecules of $Be(HO)_2$ were—

With the	1st	gram-molecule H_2SO_4	19,140 c
„	2nd	„ „	16,761
„	3rd	„ „	12,387

This behaviour calls to mind the neutralization of the tribasic acids, arsenic and phosphoric, with sodium hydroxide, for here, too, it was found that the thermal effect is greater for the first than for the second, and for the second than for the third gram-molecule of sodium hydroxide; for example, for arsenic acid the numbers are respectively 14,990, 12,590, and 8340 c. Although the agreement is possibly only accidental, it must nevertheless be noted that the difference between the heats of neutralization of beryllium hydroxide by sulphuric acid and of arsenic acid by caustic soda appears to be a constant, namely—

	1st mol.	2nd mol.	3rd mol.
Beryllium hydroxide .	19,140 c	16,761 c	12,387 c
Arsenic acid	14,990	12,590	8,340
Difference . .	4,150 c	4,171 c	4,047 c

6. *Anhydrous oxides :* PbO, HgO, Hg_2O, and Ag_2O.—The neutralization of these bases presents some peculiarities which will now be considered.

(*a*) *Lead oxide.*—The thermal effect when aqueous solutions of hydrochloric, nitric, acetic, sulphuric, and carbonic acids, and of hydrogen sulphide, react with anhydrous lead oxide will be found in the tables; in the first three cases the normal salts remain in solution, in the last three an insoluble compound is precipitated.

Lead oxide forms *basic salts* with nitric and acetic acids, of which the nitrate HO—Pb—NO_3 is very sparingly soluble; the acetate, on the other hand, is readily soluble. Whilst the thermal effect on formation of the normal nitrate in solution amounts to 17,770 c for 1 gram-molecule of PbO, the value for the basic nitrate is 16,800 c. Now since the heat of solution of the neutral nitrate is −7610 c, we must subtract this number from 17,770 c to obtain the thermal effect on neutralization, provided the nitrate is in the crystalline condition; this gives a value of 25,380 c, which is one and a half times as great as that of the formation of the basic salt from the same amount of lead. Precisely similar behaviour is shown on formation of the basic acetate; thus we find—

	Nitric acid.		Acetic acid.
PbO + 2 mol. acid	17,770 c sol.	25,380 c cryst.	15,470 c
PbO + 1 ,,	16,800 cryst.	16,800 ,,	10,440

Thus the first gram-molecule of acid produces double the thermal effect of the second, the values being 16,800 c as against 8580 c, and 10,440 c as against 5030 c, respectively, when the basic and neutral salts react under similar conditions. Lead oxide, therefore, dissolves in a solution of lead acetate with evolution of heat.

The *halides of lead* are either sparingly soluble or insoluble in water. The formation of these compounds by the interaction of lead oxide and hydrochloric, hydrobromic, and

hydriodic acids is accompanied by the following thermal effects :—

$$\left.\begin{array}{r}(PbO, 2HClAq) = 22{,}190 \text{ c} \\ (PbO, 2HBrAq) = 25{,}750 \\ (PbO, 2HIAq) = 31{,}520\end{array}\right\} \text{complete precipitation,}$$

whilst the heats of solution of $PbCl_2$ and $PbBr_2$ are, according to my direct measurements—

$$(PbCl_2, Aq = -\ 6{,}800 \text{ c}$$
$$(PbBr_2, Aq) = -10{,}040.$$

If we add these numbers to those given above, we obtain the true heats of neutralization of hydrochloric and hydrobromic acids, namely—

$$\left.\begin{array}{r}(PbO, 2HClAq) = 15{,}390 \text{ c} \\ (PbO, 2HBrAq) = 15{,}710\end{array}\right\} \text{without precipitation.}$$

These values are not only equal to one another, but agree also with the heat of neutralization of acetic acid, *i.e.* 15,470 c. If, now, we take the mean of these two numbers, namely 15,550 c, as the heat of neutralization of hydriodic acid, the heat of solution of lead iodide will be

$$(PbI_2, Aq) = -15{,}970 \text{ c.}$$

(*b*) *Oxides of mercury.*—These oxides have a very small affinity for nitric acid, as is shown by the ease with which aqueous solutions of the nitrates are decomposed on dilution with water. The thermal effects for *nitric acid* are

$$(HgO, 2HNO_3Aq) = 6400 \text{ c}$$
$$(Hg_2O, 2HNO_3Aq) = 5790,$$

whilst hydrochloric acid gives

$$(HgO, 2HClAq) = 18{,}920 \text{ c}$$
$$(Hg_2O, 2HClAq) = 30{,}070 \text{ (insol. } Hg_2Cl_2);$$

so that for HgO the thermal effect is three times as great for hydrochloric as for nitric acid.

This great difference in thermal effect is the reason that an *aqueous solution of mercuric nitrate is completely converted into chloride by the addition of an aqueous solution of hydrochloric*

acid, sodium chloride, etc. But since no precipitation results from the mixing of the two solutions, the only evidence that a reaction has taken place is given by the calorimetric measurements, which show a heat evolution of 12,520 c (experimental value 12,930 c).

This property can be utilized for *titrating a solution of mercuric nitrate*, which as a rule contains free acid. If such a solution be mixed with a solution of potassium chloride, two neutral compounds will be formed, namely, potassium nitrate and mercuric chloride, together with free nitric acid, which can be titrated directly.[1]

(*c*) *Silver oxide.*—Although in most chemical reactions silver oxide behaves as a weak base, yet nevertheless it is capable of completely neutralizing aqueous solutions of the strong acids, such as nitric and sulphuric; whilst salts of the far stronger bases of the magnesia group show a more or less strongly acid reaction in aqueous solution. Silver, in this respect, therefore, reminds us most of the alkali metals, with which some of its salts are isomorphous.

Finally, silver oxide must also be associated with thallous oxide, partly on account of its high specific gravity, partly owing to the sparing solubility of its halogen compounds. The heat of neutralization of silver oxide is, however, far smaller than that of thallous oxide, but the difference between the thermal effects for the sulphates and nitrates is the same in the two cases (see p. 136).

7. *Heats of neutralization and of solution of sparingly soluble and insoluble compounds.*—Whilst the heats of neutralization of equivalent quantities of aqueous solutions of the bases of the alkalies and alkaline earths are equal for the same acid, there is frequently a very much larger thermal effect when the salt formed is precipitated from solution. There is no reason to suppose that the true heat of neutralization would be in any

[1] Note by translator.—Mercury itself can be titrated by the addition of hydrocyanic acid to a solution of the chloride; this converts mercuric chloride into non-ionized mercuric cyanide, leaving highly ionized hydrochloric acid in solution: the latter can then be titrated with alkali.

way influenced by the degree of solubility of the compound, and we must therefore conclude that the increased evolution of heat is due to the heat of precipitation of the substance added on to its heat of neutralization. A number of specially devised experiments were carried out to confirm the accuracy of this assumption.

Thallous hydroxide in aqueous solution gives exactly the same thermal effect as the hydroxides of the alkali metals on neutralization by sulphuric or nitric acids, whilst with hydrochloric acid it gives a far higher value, since thallous chloride is precipitated. Now since thallous chloride is not absolutely insoluble in water, it is possible to measure the heat of solution directly (see *Therm. Unters.*, iii. p. 341). As a result of 22 calorimetric experiments carried out for the accurate determination of this number, it is evident that the heat of solution of 1 gram-molecule of TlCl amounts to $-10{,}100$ c. If now we add this value to the thermal effect due to the reaction between hydrochloric acid and an aqueous solution of thallous hydroxide where there is complete precipitation of TlCl— that is, to 23,840 c (p. 120)—we obtain

$$23{,}840\text{ c} - 10{,}100\text{ c} = 13{,}740\text{ c}.$$

But this is precisely the value found for the heat of neutralization of 1 gram-molecule of hydrochloric acid by aqueous solutions containing 1 gram-molecule of the hydroxides of lithium, sodium, or potassium, namely 13,780 c; there can therefore be no doubt but that the *true heat of neutralization of thallous hydroxide with hydrochloric acid is equal to that of the neutralization of the hydroxides of the alkali metals*, and that consequently the heat of solution of thallous chloride must be

$$(TlCl, Aq) = -10{,}100\text{ c}.$$

Now, since hydrochloric, hydrobromic, and hydriodic acids have equal heats of neutralization, the differences in the amount of heat evolved when a solution of thallous hydroxide reacts with these acids must be sought for in the *unequal heats of solution of the halogen compounds* formed. The last-mentioned values can be determined by subtracting from 13,740 c, which is the heat of neutralization of the acids, the thermal effect due to

the neutralization and precipitation of the halogen compounds. We thus obtain—

	Heat of neutralization.	Heat of reaction on precipitation.	Heat of solution.
for TlCl . .	13,740 c	−23,840 c =	−10,100 c = (*TlCl, Aq*)
,, TlBr . .	13,740	−27,510 =	−13,770 = (*TlBr, Aq*)
,, TlI . . .	13,740	−31,610 =	−17,870 = (*TlI, Aq*)

This important result was also confirmed in other ways.

Lead monoxide behaves similarly to thallous oxide with respect to the acids mentioned, since its halogen compounds are sparingly soluble in water; they are not, however, so insoluble as the thallium compounds, so that it was possible to make a direct estimation of the *heats of solution of both lead chloride and lead bromide.* The results were

$$(PbCl_2, Aq) = -\ 6{,}800\ \text{c}$$
$$(PbBr_2, Aq) = -10{,}049.$$

and it follows from this that hydrochloric and hydrobromic acids also show the same heat of neutralization with regard to lead oxide, namely, 15,390 c and 15,710 c respectively, which is exactly the same value that was given by acetic acid, *i.e.* 15,470 c (see p. 133).

Silver oxide is in complete agreement with thallous oxide with respect to its heat of neutralization, as will be apparent from the following comparison :—

B	(B, SO_3Aq)	(B, N_2O_5Aq)	$(B, 2HClAq)$	$(B, 2HC.Aq)$
Tl_2OAq	31,130 c	27,380 c	27,480 c	47,680 c insol.
Ag_2O	14,490	10,880	(10,910)	42,380 ,,
Difference	16,640 c	16,500 c	(16,570) c	5,300 c

The two bases thus show the same difference in heat effect when neutralized by sulphuric and nitric acids, the average value being 16,570 c; there is consequently ground for assuming that the same difference would be shown in the case of hydrochloric acid, provided the chlorides formed remained in solution. The neutralization of silver oxide by hydrochloric acid

must therefore produce a heat effect of 10,910 c. But since, when the chloride is precipitated, the heat of reaction, according to column 5, is 42,380 c, the heat of solution of silver chloride will consequently be

$$10{,}910\,c - 42{,}380\,c = -31{,}470\,c;$$

similarly that of thallous chloride is

$$27{,}480\,c - 47{,}680\,c = -20{,}200\,c.$$

In this way the following heats of solution have been obtained for the sparingly soluble or insoluble chlorides of lead, thallium, and silver:—

$PbCl_2$	− 6,800 c	TlCl	− 10,100 c	AgCl	− 15,740 c
$PbBr_2$	− 10,040	TlBr	− 13,750	AgBr	− 20,100
PbI_2	− 15,970	TlI	− 17,850	AgI	− 26,410

The sulphates of the alkaline earths are also sparingly soluble or insoluble; their heats of solution can be deduced in the following manner. Barium hydroxide solution on neutralization with hydrochloric acid gives rise to 27,780 c, but with sulphuric acid, on the other hand, it gives 36,900 c, since barium sulphate is precipitated. The difference is in this case 9120 c, whilst for the 10 other bases investigated it amounts only to 3500 c (see p. 125). We must consequently assume that this great difference is due to the *heat of precipitation of barium sulphate*, which will therefore be 5620 c. This value is in complete agreement with the thermal effect of 5615 c produced by the decomposition of the sulphates of the magnesia group with aqueous solutions of barium chloride, by which means barium sulphate is precipitated; but no thermal effect will be produced unless there is a precipitation of one of the salts formed. Similar investigations with the other alkaline earths gave the following values:—

$$(BaSO_4, Aq) = - \ 5{,}920\ c$$
$$(SrSO_4, Aq) = - \ 300$$
$$(CaSO_4, Aq) = + \ 4{,}440$$
$$(MgSO_4, Aq) = + 20{,}280$$

Comparing these results with the values found for the sparingly soluble halogen compounds, we arrive at the following conclusions: *In a group of analogous sparingly soluble or*

insoluble compounds the heat of solution rises with an increased solubility of the substance in water; that is to say, the heat effect when negative becomes less, when positive, greater.

The heats of solution of the halogen compounds referred to are negative, being least so for the chlorides, and most strongly for the iodides, which latter are the most sparingly soluble halogen compounds; and similarly the heats of solution of the sulphates decrease from the readily soluble magnesium sulphate to the almost insoluble barium sulphate.

The same behaviour is shown in the *heats of solution of hydroxides*, which, according to the numbers already communicated (Table 1), amount to

Hydroxide.	Heat of solution.
$Ba(OH)_2$	+12,260 c
$Sr(OH)_2$	+11,640
$Ca(OH)_2$	+ 2,790
$Mg(OH)_2$	0

Here also the absolute value of the heat of solution rises with the solubility.

Now since the neutralization phenomena of the bases of the magnesia group agree very closely with those of the alkaline earths, with magnesium hydroxide as the connecting link, there is every reason to suppose that the absolute heats of neutralization of the bases of the magnesia group are, similarly to those of the alkaline earths, equal to one another, and that the observed differences arise from the unequal heats of solution of the bases. If this be so, the bases of the magnesia group must have the following heats of solution :—

$Mg(OH)_2$,	0 c
$Mn(OH)_2$	− 4,800
$Ni(OH)_2$	− 5,100
$Co(OH_2$	− 6,600
$Fe(OH)_2$	− 6,300
$Zn(OH)_2$	− 7,800
$Cu(OH)_2$	−12,800

and they will then, together with the alkaline earths, form a progressive series of hydroxides in which the heat of solution rises continuously from −12,800 c to + 12,260 c.

If this supposition be correct, the neutralization phenomena of a long series of bases appear to show extremely simple relationships. Neutralization will thus be accompanied by an equal thermal effect, provided that both before and after the reaction the constituents all remain dissolved in water, and the idea has therefore arisen that aqueous solutions contain the dissolved substances in a condition which, similarly to the gaseous state, exhibits the physical properties of the substances in their simplest form, and allows of a direct comparison between them.

CHAPTER VI

PARTIAL DECOMPOSITION

In the preceding chapter we have investigated the reciprocal relations between aqueous solutions of acids and bases, and have pointed out, by means of the thermal effect accompanying the reactions, that these substances, in accordance with experience, unite together in definite proportions which are dependent upon their molecular valency, since the thermal effect on neutralization of an acid rises proportionately to the quantity of the base employed until that amount has been added which the basicity of acid requires, whilst a further increase in the amount of the base scarcely produces any appreciable change in the heat of neutralization.

The question which we shall attempt to answer in this chapter is the following: *What will happen in an aqueous solution containing two acids and one base when there is not sufficient of the latter to neutralize both acids?* We might imagine that one acid only will be neutralized, whilst the other will remain wholly or in part in the free state, and it is certainly a matter of common experience that some acids can completely expel others from their compounds. Thus hydrochloric acid can expel carbonic acid from its salts, the decomposition being complete on warming; similarly sulphuric acid can completely expel nitric acid from the nitrate of an element which forms an insoluble sulphate; but such complete decomposition is dependent solely upon certain physical conditions, namely, the volatility of an acid or the insolubility of a salt, and it is a well-established fact that it is the possibility of forming either volatile or insoluble compounds which most frequently completes a chemical reaction.

On the other hand, when the three reacting substances are soluble and remain in solution after the reaction has taken place, there is no external evidence that any reaction has occurred. The object of the following research is partly to point out that the base is divided between the two acids, partly to determine the quantitative relation of the partition.

If now we attempt to solve this problem thermochemically by investigating the thermal effect when, for instance, one acid acts upon the salt of another acid in aqueous solution, we must be careful to choose two acids with unequal heats of neutralization ; for otherwise it may happen that no thermal change is observed. But if we select, for example, sulphuric and nitric acids, in which the heats of neutralization by means of two gram-molecules of caustic soda in aqueous solution show a difference of 4020 c, then there will be an evolution of heat when sulphuric acid acts upon an aqueous solution of sodium nitrate, whilst an absorption of heat will occur in the reaction between nitric acid and sodium sulphate, provided no decomposition of the salt takes place ; the accuracy of these statements has been experimentally proved.

1. As the starting-point for the following researches I selected the relation between aqueous solutions of sodium hydroxide, and of sulphuric and nitric acids. A knowledge of the thermal effect of the following reactions is necessary for the pursuit of the investigations, namely, the thermal effect on

(1) Neutralization of sulphuric acid with sodium hydroxide.
(2) ,, ,, nitric ,, ,, ,, ,,
(3) Reaction of sulphuric acid upon sodium nitrate.
(4) ,, nitric ,, ,, sulphate.
(5) ,, sulphuric ,, ,, ,,
(6) ,, nitric ,, ,, nitrate.
(7) ,, sulphuric ,, nitric acid.

Reactions (3), (4), and (5) must be investigated for different proportions between the reacting substances, since the thermal effect changes with the relative amounts. A large number of very careful determinations had therefore to be carried out in

order to obtain accurate results. Researches on similar lines were also undertaken on the relations between hydrochloric acid, sulphuric acid, and sodium hydroxide, and these were subsequently extended to a number of other acids and bases.

Of the seven above-mentioned reactions the 6th and 7th are most frequently dispensed with, since in the reaction between nitric and sulphuric acids in dilute aqueous solution there is scarcely any perceptible thermal effect, and in the reaction between sodium nitrate and nitric acid, and similarly in that between sodium chloride and hydrochloric acid, the thermal effect is so small that only in special cases need it be taken into account; there remain therefore only the 3rd, 4th, and 5th reactions to be studied in detail.

The *reaction between sulphuric acid and sodium sulphate* gives rise to a negative thermal effect, which increases with the amount of acid. The function can be approximately expressed by the formula

$$(Na_2SO_4Aq, nSO_3Aq) = -\frac{n}{n+0{\cdot}8}3300 \text{ c}, \quad . \quad (1)$$

as will be seen by comparing the values given below for the experimental results with those calculated according to the equation

(Na_2SO_4Aq, nSO_3Aq)

	n	Experimental.	Calculated.
Table A	$\frac{1}{4}$	− 792 c	− 786 c
	$\frac{1}{2}$	−1262	−1270
	1	−1870	−1834
	2	−2352	−2356
	4	−2682	−2750

In the action of sulphuric acid upon sodium nitrate and sodium chloride I have found the following thermal effects:—

	n	$(2NaNO_3Aq, nSO_3Aq)$	$(2NaClAq, nSO_3Aq)$
Table B	1	576 c	488 c
	2	758	672

Experiments to determine the thermal effect in the reverse process, namely, the *action of nitric and hydrochloric acids upon sodium sulphate*, give the following results :—

	n	(Na_2SO_4Aq, nN_2O_5Aq)	m	$(Na_2SO_4Aq, m2HClAq)$
Table C	$\frac{1}{8}$	− 904 c		
	$\frac{1}{4}$	−1616		
	$\frac{1}{2}$	−2584	$\frac{1}{2}$	−2494 c
	1	−3504	1	−3364
	2	−4052	2	−3756
	3	−4100	4	−3792

These numbers clearly demonstrate that the action of the acids mentioned causes a marked decomposition of the sodium salts; we shall now attempt to determine the extent of this decomposition.

2. The result of the preceding determinations can be briefly summed up as follows :—

(*a*) The action of sulphuric acid upon sodium sulphate in aqueous solution produces an absorption of heat.

(*b*) The action of sulphuric acid upon sodium nitrate or sodium chloride produces an evolution of heat.

(*c*) When nitric or hydrochloric acids react with sodium sulphate an absorption of heat is observed.

All three thermal effects change proportionately to the amount of the reacting acids, and approach a maximum.

If now we compare the thermal effects for the second and third of these reactions, when equivalent quantities of acid and salt are interacting, we shall find that the differences between (*b*) and (*c*) are equal to the differences between the heats of neutralization of the acids in question by means of sodium hydroxide. Taking the values from the preceding table, where m or n are equal to 1, we find

	Difference.
$(2NaNO_3Aq, SO_3Aq) = +\ 576$	4080 c
$(Na_2SO_4Aq, N_2O_5Aq) = -3504$	
$(2NaClAq, SO_3Aq) = +\ 488$	3852 c
$(Na_2SO_4, 2HClAq) = -3364$	

whilst the differences between the heats of neutralization of sodium hydroxide by sulphuric acid and by either nitric or hydrochloric acids, respectively, are 4020 c and 3890 c (see Table 13); there is therefore complete agreement, which can be expressed in the following manner.—

The difference in thermal effect in the reaction between one equivalent of sodium nitrate and one equivalent of sulphuric acid, and in the reaction between one equivalent of sodium sulphate and one equivalent of nitric acid, is equal to the difference between the heats of neutralization of sulphuric and nitric acids. The same relation is also observed in the case of hydrochloric acid.

That this simple relation not only holds good for sodium salts, but is of universal application, is proved by the following researches on the behaviour of a large number of salts when acted upon by sulphuric and hydrochloric acids

3. The table below contains the thermal effects of the three following reactions, corresponding to the above-mentioned (*a*), (*b*), and (*c*). When *V* represents 1 gram-atom of a divalent or 2 gram-atoms of a monovalent metal, the reactions are

$$a = (VSO_4Aq,\ SO_3Aq)$$
$$b = (VCl_2Aq,\ SO_3Aq)$$
$$c = (VSO_4Aq,\ 2HClAq)$$

Table D

V	*a*	*b*	*c*	*b*−*c*
Na_2	−1870 c	+ 488 c	−3364 c	3852 c
K_2	−1648	620	−3188	3808
$(NH_4)_2$	−1412	648	−2960	3608
Mg	−1076	930	−2592	3522
Mn	− 904	1056	−2528	3584
Fe	− 896	1096	−2492	3588
Zn	− 880	1124	−2464	3588
Co	− 826	1152	−2436	3588
Ni	− 792	1132	−2382	3514
Cu	− 676	1252	−2292	3544

We see from the preceding table that for all the bases considered the thermal effect in the three reactions is of the same character as in the case of sodium hydroxide; and, furthermore, it is evident from the fifth column that the

difference $b - c$ is equal to the difference between the heats of neutralization of sulphuric and hydrochloric acids; that this is of about equal value for these bases (see pp. 125 and 129) is also shown by the numbers obtained for $b - c$, which are of approximately the same magnitude. *This result is consequently of general application, and may be theoretically proved* in the following manner:—

According to general thermochemical principles the thermal effect is the same, whether the three substances A, B, and A' act upon one another simultaneously in aqueous solution, or whether two of the substances are first allowed to interact, and then the resultant solution is exposed to the action of the third substance. In both cases the solution will ultimately contain the same compounds, and since the initial and final states are identical, the total thermal effect will also be the same. We can express this in the form of an equation (see p. 8),

$$(A, B, A') = (A, B) + (AB, A') = (A', B) + (A'B, A),$$

from which it follows

$$(AB, A') - (A'B, A) = (A', B) - (A, B) \quad . \quad . \quad . \quad (2)$$

If now for A, B, and A' we substitute

$$B = 2NaOHAq \qquad A = 2HNO_3Aq \qquad A' = H_2SO_4Aq,$$

it follows that

$$\left.\begin{matrix} +(2NaNO_3Aq, H_2SO_4Aq) \\ -(Na_2SO_4Aq, 2HNO_3Aq) \end{matrix}\right\} = \left\{\begin{matrix} +(2NaOHAq, H_2SO_4Aq) \\ -(2NaOHAq, 2HNO_3Aq) \end{matrix}\right. \quad (3)$$

or in words: The difference in thermal effect, when one equivalent of sulphuric acid reacts with one equivalent of sodium nitrate, and when one equivalent of nitric acid reacts with one equivalent of sodium sulphate in aqueous solution, is equal to the difference between the heats of neutralization of the two acids. This statement is necessarily of general application, since any other substances may be substituted for A, B, and A', provided the ultimate products of the reaction all remain in solution.

4. *The state of the solution after the reaction* of the three substances can now be deduced from the experimental results given below. The simplest relation naturally occurs when equivalent quantities of acid and base interact, as, for example, $2NaOH$, $2HNO_3$, and H_2SO_4. These three substances will then correspond to the letters A, B, and A' in equation (2). Now when Na_2SO_4 reacts with 2 molecules of HNO_3 in aqueous solution, by which means x molecules of Na_2SO_4 are decomposed and converted into $2x$ molecules of $NaNO_3$, the composition of the liquid will be

$$(1-x)BA' + xBA + xA' + (1-x)A,$$

and the resultant thermal effect will be the arithmetical sum of a series of terms corresponding to the heat changes on

(1) Decomposition of x molecules of the salt BA' or Na_2SO_4.

(2) Formation of x molecules of the salt BA or $2NaNO_3$.

(3) Reaction of x molecules of the acid A' with $(1-x)$ molecules of the salt BA'.

(4) Reaction of $(1-x)$ molecules of the acid A with x molecules of the salt BA.

(5) Reaction of x molecules of the acid A' with $(1-x)$ molecules of the acid A.

Now since, as has been previously mentioned, the last of these reactions produces no appreciable thermal effect, and the last but one is in this case of such small magnitude that it may be neglected, the thermal effect can therefore be expressed by the equation

$$(BA', A) = x[(B, A) - (B, A')] + [(1-x)BA', xA'] \quad . \quad (4)$$

But according to the values given in the Tables for A, B, and C,

$$(BA', A) = (Na_2SO_4Aq, N_2O_5Aq) = -3504 \text{ c},$$

and according to equation (2) the first difference in equation (4), namely $(B, A) - (B, A')$, is equal to

$$(Na_2SO_4Aq, N_2O_5Aq) - (Na_2N_2O_6Aq, SO_3Aq)$$
$$= -3504 \text{ c} - 576 \text{ c} = -4080 \text{ c}.$$

If now we substitute these values in equation (4), we obtain

$$-3504\ c = -x \cdot 4080\ c + (1-x)(Na_2SO_4, \frac{x}{1-x}SO_3Aq) \quad (5)$$

By means of this equation the degree of decomposition, x, can be found, since the heat of interaction of sulphuric acid and sodium sulphate is given on p. 142, Table A. The calculated values are

$$1 - x = \tfrac{1}{3}, \quad x = \tfrac{2}{3}, \quad \text{and} \quad \frac{x}{1-x} = 2,$$

or in words: *When an aqueous solution containing one equivalent of nitric acid is acted upon by one equivalent of sodium sulphate,* $\frac{2}{3}$ *of the salt is decomposed.* The composition of the liquid after the reaction will consequently be

$$\tfrac{2}{3}Na_2N_2O_6Aq + \tfrac{1}{3}Na_2SO_4Aq + \tfrac{1}{3}N_2O_5Aq + \tfrac{2}{3}SO_3Aq,$$

since $\frac{2}{3}$ of the base will be united to the nitric acid, and $\frac{1}{3}$ to the sulphuric acid. The ability of nitric acid to unite with the base is therefore twice as great as that of sulphuric acid. I have called this property the "*avidity*" *of the acid;* so that nitric acid has double the avidity of sulphuric acid with respect to sodium hydroxide.

Experiments dealing with the relation between sodium sulphate and hydrochloric acid lead to precisely similar results; since an aqueous solution of hydrochloric acid has twice as great an avidity for sodium hydroxide as has sulphuric acid; an equivalent of hydrochloric acid displaces $\frac{2}{3}$ of an equivalent of sulphuric acid from its sodium salt.

5. It still remains to be seen whether the relative *avidity* is a constant when two acids are mixed in varying proportions, and whether it is the same towards other bases as towards sodium hydroxide. I shall first attempt to answer the last question.

In Table D above I have already given three series of experimental results bearing on this point, namely, the determination of the thermal effect when sulphuric acid acts upon equivalent quantities of the sulphates of 10 bases; next,

the effect when sulphuric acid acts upon the chlorides of these bases; and finally, when hydrochloric acid reacts with the sulphates of the same bases. It is evident from these investigations that the difference $b - c$ between the thermal effect of the last two reactions, as we were justified in expecting (see p. 145), is again equal to the difference between the heats of neutralization of sulphuric and hydrochloric acids by the same base. Now, in order to calculate the degree of decomposition of certain other salts in the same way as we have done above for the salts of sodium, a few additional experiments were necessary, namely, the determination of the thermal effect of the reaction between non-equivalent amounts of the sulphate and sulphuric acid. This investigation was undertaken for about half of the bases, with the following results:—

(VSO_4Aq, nSO_3Aq)

Table E

V	$n = 1$	$n = 1{\cdot}5$	$n = 2$
Na_2	−1870 c	—	−2352 c
K_2	−1648	—	−2220
$(NH_4)_2$	−1412	—	−1870
Mg	−1076	−1230 c	—
Zn	− 880	−1050	—
Cu	− 676	− 810	—

Calculations similar to those already carried out for the sodium salts lead to the results given below, where x, as before, represents that fraction of the base in question which is decomposed by an equivalent quantity of hydrochloric acid, and $\frac{1-x}{x}$ is the ratio between the *avidities* of sulphuric and hydrochloric acids for the metal of the base under consideration.

TABLE 15A.

DEPENDENCE OF AVIDITY UPON THE NATURE OF THE BASE.

V	x	$\frac{1-x}{x}$
Na_2	0·666	0·50
K_2	0·636	0·57
$(NH_4)_2$	0·640	0·56
Mg	0·590	0·70
Mn	0·586	0·71
Fe	0·573	0·74
Zn	0·577	0·73
Co	0·566	0·77
Ni	0·563	0·78
Cu	0·553	0·81

It is therefore evident from the table above that in the reaction

$$(VSO_4Aq, 2HClAq)$$

where the radical of the base is represented by V, x molecules of the salt will be decomposed. But whilst $\frac{2}{3}$ of the sodium sulphate is decomposed, the decomposition of the copper sulphate amounts only to $\frac{5}{9}$; or in other words: *The ratio of the avidity of sulphuric acid to that of hydrochloric acid rises from* 0·5 *for sodium sulphate to* 0·8 *for copper sulphate.* The relative avidity of the two acids does not differ very much in the case of the soluble bases having an average value of 0·54, nor again with regard to the magnesia series, where it averages 0·75; but the two groups of bases differ very widely from each other with respect to the magnitude of their avidities.

In all these cases we were dealing with equivalent quantities of acid and salt; but it still remains to be seen whether the avidity remains constant or whether it changes with the amount of the reacting substances when these are not present in equivalent proportions. The answer to this question has been furnished by C. M. Guldberg, who has published mathematical researches on the subject.[1]

[1] *Etudes sur les affinités chimiques*, by C. M. Guldberg and P. Waage. Christiania, 1867.

6. *Guldberg's* theory can, for our special purpose, be expressed as follows: When the (double) decomposition of two substances P and Q gives rise to the formation of the substances R and S, these substances, which are all present at the same time in equivalent proportions and are represented respectively by the letters α, β, γ, δ, will after interaction form a solution which contains

$$(a - x)P + (\beta - x)Q + (\gamma + x)R + (\delta + x)S. \quad (6)$$

where x represents the amount of substance transformed. When, for example, P represents sodium sulphate and Q nitric acid, then R will be sulphuric acid and S sodium nitrate. Before the reaction we shall therefore have

$$\alpha Na_2SO_4Aq + \beta N_2O_5Aq + \gamma SO_3Aq + \delta 2NaNO_3,$$

and after the decomposition

$$\left.\begin{array}{l}(\alpha - x)Na_2SO_4Aq + (\gamma + x)SO_3Aq \\ (\beta - x)N_2O_5Aq + (\delta + x)2NaNO_3Aq\end{array}\right\}, \quad (7)$$

when x molecules of sodium sulphate have been decomposed. If now we put k equal to the amount of the reaction $(Na_2SO_4Aq,\ 2HNO_3Aq)$ which has taken place and $\frac{1}{k_1}$ equal to the reverse reaction $(2NaNO_3Aq,\ H_2SO_4Aq)$, we shall, according to Guldberg's theory, have the following relation :—

$$k(\alpha - x)(\beta - x) = \frac{1}{k_1}(\gamma + x)(\delta + x), \quad (8)$$

from which x can be found if k and k_1 or the product kk_1, which can be expressed as c_2, are known. The magnitude c is thus a constant for all values of α, β, γ, δ. If now in the reaction $(Na_2SO_4Aq,\ 2HNO_3Aq)$ we put

$$\alpha = \beta = 1$$
$$\gamma = \delta = 0,$$

the equation will become

$$c_2(1 - x)_2 = x_2 \text{ or}$$
$$c = \frac{x}{1 - x} = \frac{\frac{2}{3}}{1 - \frac{2}{3}} = 2,$$

where $x = \frac{2}{3}$ as has been found above. If then we put kk_1 or c_2 in equation (8) equal to 4, and solve for x, we find

$$x = \tfrac{1}{6}\Big(4(\alpha+\beta)+\gamma+\delta - \sqrt{[4(\alpha+\beta)+\gamma+\delta]^2 - 12(4\alpha\beta-\gamma\delta)}\Big) \quad (9)$$

This equation therefore gives us the degree of decomposition, x, for all proportions of the four substances P, Q, R, and S. In order to determine accurately how far this formula is in accordance with facts, a large number of control experiments of the thermal effects for different values of α, β, γ, δ were undertaken, and the theoretical and experimental values for x were compared (*Therm. Unters.*, i. 118, *et seq.*). Here I shall only point out the agreement in the simplest case, namely, in the reaction

$$(Na_2SO_4,\ \beta N_2O_5 Aq),$$

where α is equal to 1, and γ and δ are equal to zero. Equation (9) will then become

$$x = \tfrac{2}{3}(1+\beta - \sqrt{(1+\beta)_2 - 3\beta}).$$

The corresponding thermal results will be found in Table C, p. 143, in which β varies from $\frac{1}{8}$ to 3. From these values of β we can calculate the value of x, and the thermal effect for the several experiments will then be

$$(Na_2SO_4 Aq,\ \beta N_2O_5 Aq) = \begin{cases} -x\,.\,4080\text{ c} - x(\beta - x)78\text{ c} \\ +(1-x)(Na_2SO_4 Aq,\ \dfrac{x}{1-x}SO_3 Aq). \end{cases}$$

The value -78 c corresponds to the reaction between 2 gram-molecules of nitric acid and 2 gram-molecules of sodium nitrate. Knowing the value of $(1-x)(Na_2SO_4 Aq,\ \frac{x}{1-x}H_2SO_4 Aq)$, which can be derived from equation (5) and is expressed in the table as r, we have the following thermal effect for the reaction $(Na_2SO_4 Aq,\ \beta\ 2HNO_3 Aq)$:—

β	x	$-x(\beta - x)78$	r	$(Na_2SO_4Aq, \beta N_2O_5Aq)$	
				Calculated	Experimental
$\frac{1}{8}$	0·121	− 0·04 c	−424 c	− 916 c	− 904 c
$\frac{1}{4}$	0·232	− 0·3	−694	−1640	−1616
$\frac{1}{2}$	0·423	− 3	−910	−2637	−2584
1	0·667	− 17	−784	−3520	−3504
2	0·845	− 76	−446	−4020	−4052
3	0·903	−147	−296	−4127	−4100

The agreement between calculated and experimental results is most satisfactory, and was shown in all the experiments described above. Hence it follows that the value c or $\sqrt{kk_1}$ is a constant, no matter what are the relative proportions of the reacting substances. But c is simply the ratio of the avidities of nitric and sulphuric acids towards sodium hydroxide. The results therefore justify the following statement, that *the ratio between the avidities of two acids is a constant for one and the same base.*

7. It has now been proved that the degree of partial decomposition of a salt by an acid other than that present in the salt is dependent upon the relative amounts of the acids, and also upon a constant magnitude known as the relative avidity of the acids; this latter, as has already been stated, expresses the ratio in which a base is distributed between two acids when the three substances are present in equivalent proportions. It still remains to be determined whether the avidity is in any way influenced by the degree of dilution of the liquid, and by its temperature.

In order to answer this question I made a great many calorimetric experiments on partial decomposition, in which the dilution varied from 1 to 2 and 4; some of these experiments were carried out at a temperature of about 7·5°, others at about 25°, whilst the experiments already described took place at about 18°. As a result of these experiments, which will be described in a subsequent chapter, it is evident that whilst the actual thermal effects under the several conditions are appreciably influenced by the temperature and degree of dilution, yet nevertheless the ratio in which the base is distributed between the two acids remains unchanged; or in other words,

the relative avidities of the acids are independent of the degree of dilution of the liquid, and of its temperature. Furthermore, it has already been shown that the relative avidities of two acids can be determined by the ratio in which a base is distributed between them, this value being in no way influenced by the concentration of the acids; it is therefore clear that the avidity is a specific property of an acid, and that it determines the strength with which the acid will react in aqueous solution. It was consequently desirable to measure the avidities of a large number of acids, and I have succeeded in accomplishing this for about half of those acids of which I have already investigated the neutralization phenomena. Particulars of these experiments will be found in *Therm. Unters.*, i. 150–309.

8. The results of my researches on *relative avidities of acids* are given in the following Table, 15B. The avidity of hydrochloric acid was taken as the unit, and all values refer to the reaction with sodium hydroxide.

TABLE 15B.

Relative Avidity of Acids.			Table giving Relative Avidities measured by—[1]		
	Acid.	Avidity.	Electric conductivity.	Hydrolysis of methyl-acetate.	Inversion of cane sugar.
			I.	II.	III.
1 mol.	Nitric acid	1·00	0·996	0·92	1·00
1 ,,	Hydrochloric acid .	1·00	1·00	1·00	1·00
1 ,,	Hydrobromic acid .	0·89	1·01	0·98	1·11
1 ,,	Hydriodic acid . .	0·79	—	—	—
½ ,,	Sulphuric acid . .	0·49	0·65	0·74	0·73
½ ,,	Selenic acid . . .	0·45	—	—	—
1 ,,	Trichloracetic acid .	0·36	0·62	0·68	0·73
1 ,,	Orthophosphoric acid	0·25	0·07	—	0·06
½ ,,	Oxalic acid . . .	0·24	0·20	0·17	0·18
1 ,,	Monochloracetic acid	0·09	0·05	0·04	0·05
1 ,,	Hydrofluoric acid .	0·05	—	—	—
½ ,,	Tartaric acid . . .	0·05	0·023	0·023	—
⅓ ,,	Citric acid	0·05	0 017	0·016	0·017
1 ,,	Acetic acid . . .	0·03	0·004	0·003	0·004
½ ,,	Boracic acid, B_2O_3 .	0·01	—	—	—
½ ,,	Silicic acid . . .	0·00	—	—	—
1 ,,	Hydrocyanic acid .	0·00	—	—	—

[1] Note by translator.—It must be explained that the first three columns only of this table comprise Thomsen's table, 15B. The numbers in the

These numbers prove that the avidities of acids vary considerably in magnitude. The highest values were found equally for nitric and hydrochloric acids, the avidity in this case being put equal to 1. Next in value are hydrobromic and hydriodic acids, which are respectively equal to 0·9 and 0·8; then follow sulphuric and selenic acids with a value of 0·5, whilst for orthophosphoric and oxalic acids, the avidity is only 0·25. The differences in the avidities of trichloracetic, monochloracetic, and acetic acids are especially noteworthy, and are in the ratio 0·36 : 0·09 : 0·03; for silicic and hydrocyanic acids the value is approximately equal to zero, since these acids can be completely replaced in their sodium salts by equivalent amounts of the majority of other acids. The avidity does not appear to be proportional to any other property of the acid; it is in every case *entirely independent of the heat of neutralization;* for example, for hydrofluoric acid, which has been shown to have the highest heat of neutralization, the avidity is only one-twentieth of that of hydrochloric acid.

9. *The general results* of my researches on partial decomposition in aqueous solution, the object of which was to show in what proportion a base is distributed between two acids existing simultaneously in solution when the amount of the base is insufficient for the neutralization of both acids, can be summed up as follows:—

(*a*) When nitric or hydrochloric acids react with aqueous solutions of sulphates an *absorption of heat* is observed, which rises with the amount of acid, but decreases as the basic element becomes less electropositive in the series: Na_2, K_2, $(NH_4)_2$, Mg, Mn, Fe, Zn, Co, Ni, and Cu.

(*b*) In the reverse reaction, when sulphuric acid acts upon solutions of nitrates and chlorides, an *evolution of heat* is observed, which also rises with the amount of acid, but on the

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last three columns, which are not found in the Danish work, are introduced for purpose of comparison, and show that, as far as order of magnitude is concerned, there is a remarkable agreement between the relative avidities as determined by four different methods.

[1] See translator's preface.

other hand decreases as the basic element becomes less electropositive.

(*c*) When in the one case one equivalent of the acid A' reacts with one equivalent of the salt BA, and in the other case one equivalent of the acid A reacts with one equivalent of the salt AB', the difference in thermal effect in the two cases will be equal to the difference in the heats of neutralization of the two acids with respect to the base B. This proves that in the two cases the resulting solution is of precisely the same composition, and that a partial decomposition of the salt has taken place in such a manner that the solution now contains two salts and two free acids. Provided there were no side-reactions, the magnitude of the thermal effect in the reactions described under 1 and 2 would be proportional to the degree of partial decomposition; but the action of the free acids upon their respective salts introduces other thermal effects which interfere with the proportionality.

(*d*) Thus in the reaction between aqueous solutions of sulphuric acid and of sulphates an absorption of heat is observed, which rises with the amount of acid, but falls as the basic element is less electropositive.

(*e*) The degree of partial decomposition—that is to say, the distribution of the base between two acids—can, in each special case, be deduced from the observed thermal effects. The ratio in which the base is distributed between the two acids when the three substances are present in equivalent proportions is known as the *relative avidity of the acid.*

(*f*) The relative avidity of two acids is a *constant* magnitude, which determines the degree of decomposition of the acids when reacting with one and the same base; but the relative avidity *changes with the nature of the base.* Thus the ratio of the avidities of hydrochloric and sulphuric acids towards caustic soda is as 1 : 0·5, whilst the ratio of the avidities of the same acids towards copper oxide is as 1 : 0·8. The avidity of sulphuric acid therefore rises as we proceed from sodium to copper in given series.

(*g*) The avidity of acids differs very widely. It is greatest, and of equal value, for hydrochloric and nitric acids; less for

the majority of organic acids, and practically equal to zero for silicic and hydrocyanic acids; but it does not, however, bear any simple relation to the heats of neutralization or to the basicity of the acids.

(*h*) The avidity has been shown to be *independent of the concentration* when the solution formed contains from 100 to 400 molecules of water for each molecule of the salt (for example, Na_2SO_4), and it was also *independent of the temperature* between the experimental limits of 7° and 25°. In all cases the ratio in which the base was distributed between the acids was the same.

CHAPTER VII

THE INFLUENCE OF TEMPERATURE UPON THE MAGNITUDE OF THE THERMAL EFFECT OF CHEMICAL PROCESSES

THE thermal effect of a chemical reaction is not a constant magnitude, since it is dependent not only upon the temperature, but also upon the state of aggregation and other conditions under which the substances react, as, for instance, upon the degree of dilution.

In the following chapter I shall describe my researches upon the influence of temperature on the thermal effect due to chemical reactions, with special reference to aqueous solutions. The majority of thermochemical data are derived from reactions carried out in solution, since as a rule they give more accurate results than processes carried out with dry substances.

The results obtained are, however, only valid at the actual temperature of the experiment; and in order that the determinations may be comparable among themselves, and also with those of other processes, it is necessary that all ordinary measurements should be made at approximately the same temperature. I therefore selected from 18° to 20° C. as the most convenient temperature for the experiments.

In order to utilize the direct measurements for the determination of the thermal effects at other temperatures, a knowledge of the *specific heats* of the different solutions is indispensable, and I consequently undertook the determination of this value for those aqueous solutions which are most frequently employed. The present chapter is therefore divided into the following sections :—

(*a*) Experimental results of the specific heats of aqueous solutions at 18° to 20° C.;

(*b*) Direct experiments upon the influence of temperature on the heats of neutralization;

(*c*) Dependence of the thermal effect upon the specific heat of the solution employed;

(*d*) Influence of temperature upon the heats of solution of substances;

(*e*) Influence of temperature upon the thermal effect on dilution of aqueous solutions; and

(*f*) Influence of temperature upon the thermal effect on partial decomposition in aqueous solutions, and upon its degree.

All these researches are closely connected with a long series of investigations upon the specific heats of aqueous solutions, which will first be described.

A. Numerical Results of Experiments upon the Specific Heats and Densities of Aqueous Solutions at from 18° to 20° C.

When, in the year 1870, I resolved to undertake this research, there already existed certain experimental data on the subject; but the experiments had been carried out in a variety of different ways, and many of them in a manner which could hardly be expected to give trustworthy results, so that their use would be likely to introduce appreciable errors into the calculations. It was therefore necessary to measure the specific heats at a definite temperature, or rather, over a temperature interval of from 2 to 3 degrees, whilst the results of the earlier experimenters may be taken as the mean specific heats over a much wider range of temperature.

The following method was adopted: *About* 1000 *grams of the solution under consideration was warmed in a calorimeter by means of the heat evolved on burning a definite volume of hydrogen.* The conditions were so arranged that the temperature of the liquid was only increased by about 3°, so that the influence of the surroundings was reduced to a minimum. In

this manner the specific heats were found for a very small temperature interval, whilst the results of the earlier experimenters ranged over 40° or 50°.

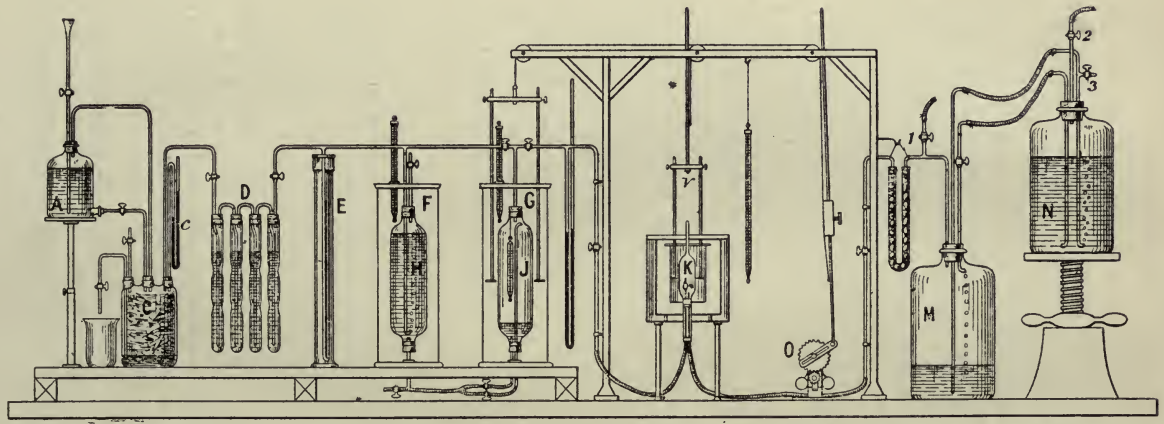
The apparatus employed, though somewhat complicated in structure, is well adapted to the purpose and gives trustworthy results ; it is described in detail, together with the method of working, in *Therm. Unters.*, i. pp. 27 to 35, where will also be found the original diagram of the apparatus reproduced in Fig. 7. Here I shall consider only the magnitude of the source of heat —that is, the heat of combustion of the volume of hydrogen used, which was measured in a number of experiments in which the calorimeter contained 900 grams of water. The heat of combustion of the given (absolute) volume of hydrogen was $2649\ c \pm 4\ c$; the rise of temperature is therefore about 3°. The following tables contain the results of 216 calorimetric experiments, but the experimental details are omitted.

At the same time that the specific heats were determined I also measured the *specific gravities* of the solutions employed, so that besides the *molecular heats* the tables also include the *molecular volumes* of the solutions under investigation. If we call the molecular weight M, the specific heat s, and the specific gravity p, we shall have

$$\text{Molecular heat} = s \,.\, M$$

$$\text{Molecular volume} = \frac{M}{p}$$

For the correct interpretation of the numbers in the table given below, the following general remarks are necessary. The composition of the solution may be expressed by the formula $M + nH_2O$, which means that for every molecule of substance there are n molecules of water. In the *first* column n expresses the amount of water in the solution; the *second* column gives the experimental values of the *specific heats;* the *third* the molecular weights of the solutions, the molecular weights of the substances and of the water being given separately, so as to render the results more obvious ; the *fourth* column contains the molecular heats, which are the product of the numbers in the second and third columns, and express the



A, C. Hydrogen generator.
A. Contains HCl.
C. Contains zinc.
c. Mercury manometer.
D. Tubes for purifying and drying gas; containing KOH, $CaCl_2$, etc.
E Pressure regulator; containing water.
F, G. Glass cylinders filled with water for maintaining a constant temperature in H, J.
H, J. Water gasometer for collecting hydrogen and measuring its volume.
K. Calorimeter and combustion chamber, surrounded by double-walled outer vessel.
v. Stirring apparatus.
O. Motor for driving stirrer.
M, N. Gas-holders for storing oxygen over water.
1. Tap in connection with oxygen generator.
2. Tap in connection with water pump.
3. Tap opening to atmosphere.

FIG. 7.—Apparatus for measuring the specific heats of aqueous solutions by burning a known volume of hydrogen.

number of thermal units (referred to a gram of water at 18°) required to heat a gram-molecule of each solution through 1° C.; the *fifth* column gives the differences between the molecular heats of the solutions and that of n molecules of water.

The *last three columns* in the table contain the *specific gravities* of the solutions; their molecular volumes, which are equal to the ratio between their molecular weights and densities, and represent the number of cubic centimetres which a gram-molecule of the solution occupies; and finally, in the last column are found the differences between the molecular volumes of the solutions and of the water which they contain. All specific-gravity determinations refer to a temperature of 18° C.

TABLE 16.

Specific Heats and Densities of Aqueous Solutions.

Amount of water n	Specific heat s	Molecular weight $a+b$	Molecular heat $C=s(a+b)$	Difference $C-b$	Density p	Molecular volume $R=\frac{1}{p}(a+b)$	Difference $R-b$
			Sulphuric Acid, $SO_3 + nH_2O$.				
5	0·545	80 + 90	92·7	+ 2·7	1·4722	115·5	+25·5
10	0·700	80 + 180	182·0	+ 2·0	1·2870	202·0	+22·0
20	0·821	80 + 360	361·2	+ 1·2	1·1593	379·6	+19·6
50	0·918	80 + 900	900	0	1·0692	916·6	+16·6
100	0·956	80 + 1800	1797	− 3	1·0355	1815·5	+15·5
200	0·977	80 + 3600	3595	− 5	1·0180	3614·9	+14·9
			Nitric Acid, $HNO_3 + nH_2O$.				
10	0·768	63 + 180	186·6	+ 6·6	1·1542	210·5	+30·5
20	0·849	63 + 360	359·1	− 0·9	1·0851	389·8	+29·8
50	0·930	63 + 900	896	− 4	1·0360	929·5	+29·5
100	0·963	63 + 1800	1794	− 6	1·0185	1829·2	+29·2
200	0·982	63 + 3600	3597	− 3	1·0094	3629·0	+29·0
			Hydrochloric Acid, $HCl + nH_2O$.				
10	0·749	36·5 + 180	162·2	−17·8	1·0832	199·9	+19·9
20	0·855	36·5 + 360	338·9	−21·9	1·0456	379·2	+19·2
50	0·932	36·5 + 900	873	−27	1·0193	918·8	+18·8
100	0·964	36·5 + 1800	1770	−30	1·0100	1818·5	+18·5
200	0·979	36·5 + 3600	3561	−39	1·0052	3617·7	+17·7

Amount of water n	Specific heat s	Molecular weight $a+b$	Molecular heat $C=s(a+b)$	Difference $C-b$	Density ϕ	Molecular volume $R=\frac{1}{\phi}(a+b)$	Difference $R-b$
Tartaric Acid, $C_4H_6O_6 + nH_2O$.							
10	0·745	150 + 180	246	+66	1·2409	265·9	+85·9
25	0·856	150 + 450	513	+63	1·1229	534·3	+84·3
50	0·911	150 + 900	957	+57	1·0677	983·4	+83·4
100	0·952	150 + 1800	1856	+56	1·0358	1882·5	+82·5
200	0·975	150 + 3600	3656	+56	1·0186	3681·3	+81·3
Sodium Hydroxide, $NaOH + nH_2O$.							
7·5	0·847	40 + 135	148·2	+13·2	1·2576	139·2	+ 4·2
15	0·878	40 + 270	272·2	+ 2·2	1·1450	270·7	+ 0·7
30	0·919	40 + 540	533	− 7	1·0782	537·9	− 2·1
50	0·942	40 + 900	885	−15	1·0486	896·4	− 3·6
100	0·968	40 + 1800	1781	−19	1·0246	1795·9	− 4·1
200	0·983	40 + 3600	3578	−22	1·0124	3594·8	− 5·2
Potassium Hydroxide, $KOH + nH_2O$.							
30	0·876	56 + 540	522	−18	1·0887	547·5	+ 7·5
50	0·916	56 + 900	876	−24	1·0550	906·3	+ 6·3
100	0·954	56 + 1800	1770	−30	1·0284	1804·9	+ 4·9
200	0·975	56 + 3600	3565	−35	1·0144	3604·1	+ 4·1
Ammonium Hydroxide, $NH_4OH + nH_2O$.							
30	0·997	35 + 540	573	+33	0·9878	582·1	+42·1
50	0·999	35 + 900	934	+34	0·9927	941·9	+41·9
100	0·999	35 + 1800	1833	+33	0·9967	1841·2	+41·2
Sodium Chloride, $NaCl + nH_2O$.							
10	0·791	58·5 + 180	188·5	+ 8·5	1·1872	200·9	+20·9
20	0·863	58·5 + 360	361·0	+ 1·0	1·1033	379·3	+19·3
30	0·895	58·5 + 540	536	− 4	1·0718	558·4	+18·4
50	0·931	58·5 + 900	892	− 8	1·0444	917·8	+17·8
100	0·962	58·5 + 1800	1788	−12	1·0234	1816·1	+16·1
200	0·978	58·5 + 3600	3578	−22	1·0118	3616·0	+16·0
Potassium Chloride, $KCl + nH_2O$.							
15	0·761	74·6 + 270	262·4	− 7·6	1·1468	300·4	+30·4
30	0·850	74·6 + 540	522·4	−17·4	1·0800	569·0	+29·0
50	0·904	74·6 + 900	881	−19	1·0496	928·2	+28·2
100	0·948	74·6 + 1800	1775	−25	1·0258	1827·3	+27·3
200	0·970	74·6 + 3600	3565	−35	1·0136	3625·0	+25·0

Amount of water n	Specific heat s	Molecular weight $a+b$	Molecular heat $C=s(a+b)$	Difference $C-b$	Density p	Molecular volume $R=\frac{1}{p}(a+b)$	Difference $R-b$
			AMMONIUM CHLORIDE, $NH_4Cl + nH_2O$.				
7·5	0·760	53·5+ 135	143·3	+ 8·3	1·0718	175·9	+40·9
10	0·778	53·5+ 180	181·6	+ 1·6	1·0664	219·0	+39·0
25	0·881	53·5+ 450	443·6	− 6·4	1·0314	488·2	+38·2
50	0·937	53·5+ 900	893	− 7	1·0167	937·8	+37·8
100	0·966	53·5+1800	1791	− 9	1·0086	1837·7	+37·7
200	0·982	53·5+3600	3588	−12	1·0044	3637·6	+37·6
			SODIUM NITRATE, $NaNO_3 + nH_2O$.				
10	0·769	85 + 180	203·8	+23·8	1·2474	212·5	+32.5
25	0·863	85 + 450	461·7	+11·7	1·1137	480·4	+30·4
50	0·918	85 + 900	904	+ 4	1·0600	929·2	+29·2
100	0·950	85 + 1800	1791	− 9	1·0311	1828·2	+28·2
200	0·975	85 + 3600	3593	− 7	1·0160	3627·0	+27·0
			POTASSIUM NITRATE, $KNO_3 + nH_2O$.				
25	0·832	101 + 450	458·4	+ 8·4	1·1228	490·7	+40·7
50	0·901	101 + 900	902	+ 2	1·0651	939·8	+39·8
100	0·942	101 + 1800	1701	− 9	1·0336	1839·2	+39·2
200	0·966	101 + 3600	3575	−25	1·0173	3638·3	+38·3
			AMMONIUM NITRATE, $NH_4NO_3 + nH_2O$.				
5	0·697	80 + 90	118·7	+28·7	1·2046	141·1	+51·1
20	0·859	80 + 360	378·0	+18	1·0743	409·6	+49·6
50	0·929	80 + 900	910	+10	1·0331	948·6	+48·6
100	0·962	80 + 1800	1808	+ 8	1·0180	1846·8	+46·8
			SODIUM CARBONATE, $Na_2CO_3 + nH_2O$.				
50	0·896	106 + 900	901	+ 1	1·1131	903·8	+ 3·8
100	0·933	106 + 1800	1778	−22	1·0593	1799·3	− 0·7
200	0·958	106 + 3600	3550	−50	1·0306	3596·0	− 4·0
			SODIUM SULPHATE, $Na_2SO_4 + nH_2O$.				
65	0·892	142 + 1170	1170	0	1·1010	1191·6	+21·6
100	0·920	142 + 1800	1787	−13	1·0675	1819·5	+19·5
200	0·955	142 + 3600	3574	−26	1·0350	3615·4	+15·4
			AMMONIUM SULPHATE, $(NH_4)_2SO_4 + nH_2O$.				
30	0·820	132 + 540	551	+11	1·1148	602·8	+62·8
50	0·871	132 + 900	899	− 1	1·0774	957·6	+57·6
100	0·924	132 + 1800	1785	−15	1·0420	1854·1	+54·1
200	0·959	132 + 3600	3579	−21	1·0214	3653·8	+53·8

Amount of water n	Specific heat s	Molecular weight $a+b$	Molecular heat $C=s(a+b)$	Difference $C-b$	Density ρ	Molecular volume $R=\frac{1}{\rho}(a+b)$	Difference $R-b$
			Magnesium Sulphate, $MgSO_4 + nH_2O$.				
20	0·744	120 + 360	357	− 3	1·2864	373·1	+13·1
50	0·857	120 + 900	874	−26	1·1253	906·4	+ 6·4
100	0·917	120 + 1800	1761	−39	1·0649	1803·0	+ 3·0
200	0·952	120 + 3600	3541	−59	1·0334	3599·8	− 0·2
			Sodium Acetate, $NaC_2H_3O_2 + nH_2O$.				
20	0·844	82 + 360	391	+31	1·0993	402·1	+42·1
50	0·938	82 + 900	921	+21	1·0442	940·2	+40·4
100	0·965	82 + 1800	1817	+17	1·0230	1839·7	+39·7
200	0·983	82 + 3600	3620	+20	1·0120	3638·3	+38·3
M			$M + 200H_2O$.				
KBr	0·962	119 + 3600	3758	−22	1·0236	3633	+33
NH_4Br	0·968	98 + 3600	3580	−20	1·0154	3642	+42
NaI	0·954	150 + 3600	3578	−22	1·0318	3634	+34
KI	0·950	166 + 3600	3578	−22	1·0355	3644	+44
NH_4I	0·963	145 + 3600	3606	+ 6	1·0248	3654	+54
$BaCl_2$	0·932	208 + 3600	3549	−51	1·0502	3626	+26
$CaCl_2$	0·957	111 + 3600	3551	−49	1·0253	3619	+19
K_2SO_4	0·940	174 + 3600	3548	−52	1·0380	3636	+36
$ZnSO_4$	0·947	161 + 3600	3562	−38	1·0455	3598	− 2
$FeSO_4$	0·951	152 + 3600	3568	−32	1·0413	3603	+ 3
$CuSO_4$	0·953	159 + 3600	3583	−17	1·0444	3599	− 1
$Ba(NO_3)_2$	0·933	261 + 3600	3602	+ 2	1·0584	3648	+48
$Pb(NO_3)_2$	0·919	331 + 3600	3613	+13	1·0771	3649	+49

B. Theoretical Results.

1. Molecular Heats and Molecular Volumes.

The general character of the results of this research are most clearly brought out by a survey of the figures in the fifth and eighth columns, since all the solutions investigated show the same phenomenon, namely, that *both of the values referred to decrease when the degree of dilution increases.*

In the fifth column are recorded the differences between the

molecular heats, or, as they are sometimes called, the calorific equivalents, of the solutions and those of the amount of water they contain. For sulphuric acid with 5 gram-molecules of water, the molecular heat of the solution is only 2·7 c greater than that of the solvent water; if the amount of the latter increases, the molecular heat becomes smaller: for 200 gram-molecules of water it is −5 c. This behaviour is repeated for all the other solutions; for some substances the difference is negative, even at the highest degree of concentration, as, for instance, for hydrochloric acid, potassium hydroxide, and potassium chloride, and becomes more strongly negative on greater dilution; for other solutions it is strongly positive for the concentrated solution, but similarly becomes less so on dilution.

From this property we can deduce the following general result: *When an aqueous solution is diluted with water, the molecular heat of the solution formed is less than the sum of that of the original solution together with that of the water.*

Precisely the same relation is observed with respect to *molecular volumes*. In column 8 it is shown that the difference between the molecular volume of a solution and that of the volume of water present decreases with increasing dilution, whence it follows that: *When an aqueous solution is diluted with still more water a contraction is observed, since the resulting solution occupies a smaller volume than that of the original solution together with that of the water used in dilution.*

These relations suggest a very close connection between the specific heat and the density of a given solution. A further confirmation of this conclusion can be obtained by a comparison of the molecular heats and molecular volumes of two solutions with those of the solution resulting from their mixture. We will take as an example the mixture of a solution of an acid with that of an alkali.

From the numbers contained in the tables it is evident, for example, that the *molecular heats* of solutions of sulphuric, nitric, and hydrochloric acids, and of sodium, potassium, and

ammonium hydroxides, with 100 gram-molecules of water, are as follows :—

$R=$	Na	K	NH_4
$2(ROH + 50H_2O)$	1770 c	1752 c	1868 c
$SO_3 + 100H_2O$	1797	1797	1797
Sum	3567	3549	3665
$R_2SO_4 + 201H_2O$	3592	3566	3597
Difference	+25	+17	−68
$ROH + 100H_2O$	1781	1770	1833
$HNO_3 + 100H_2O$	1794	1794	1794
Sum	3575	3564	3627
$RNO_3 + 201H_2O$	3611	3593	3624
Difference	+36	+29	−3
$ROH + 100H_2O$	1781	1770	1833
$HCl + 100H_2O$	1770	1770	1770
Sum	3551	3540	3603
$RCl + 201H_2O$	3596	3583	3606
Difference	+45	+43	+3

These results can be expressed in words : *On neutralization of equivalent solutions, of equal concentration, of the three acids and of the three bases under consideration, the molecular heat of the solution formed will in the case of potassium and sodium hydroxides be greater than that of its constituents, in the case of ammonium hydroxide, on the other hand, it will be less.*

The *molecular volumes* of these same liquids, which are also to be found in the tables, show a precisely similar relationship.

$R =$	Na	K	NH_4
$2(ROH + 50H_2O)$	1793	1813	1884
$SO_3 + 100H_2O$	1815	1815	1815
Sum	3608	3628	3699
$R_2SO_4 + 201H_2O$	3633	3654	3672
Difference	+25	+26	−27
$ROH + 100H_2O$	1796	1805	1841
$HNO_3 + 100H_2O$	1829	1829	1829
Sum	3625	3634	3670
$RNO_3 + 201H_2O$	3645	3656	3664
Difference	+20	+22	−6
$ROH + 100H_2O$	1796	1805	1841
$HCl + 100H_2O$	1818	1818	1818
Sum	3614	3623	3659
$RCl + 201H_2O$	3634	3643	3656
Difference	+20	+20	−3

It therefore follows that: *On neutralization of solutions of the hydroxides of sodium and potassium an expansion takes place; on neutralization of ammonium hydroxide solution, on the other hand, there is a contraction.*

The agreement between the numbers in these two tables is so striking and so convincing that there can be no doubt but that a *close connection exists between the specific heat of a solution and its density.*

2. Influence of Temperature upon the Heat of Neutralization.

In order to ascertain the influence of temperature upon the heat of neutralization, I undertook during the winter of 1873 some direct experiments at temperatures differing from each other by intervals of 15° to 17° C.; namely, partly at the ordinary room temperature of 7° to 9°, and partly after the temperature had been raised to 25°. The atmospheric conditions

did not allow of a lower temperature than about 7° being maintained in the laboratory, and a higher temperature than about 25° would naturally be unendurable for the length of time occupied by the observations.

The neutralization experiments were carried out with the same liquids and the same apparatus, and, excepting that the temperature of the reactions was different, under exactly similar conditions. The researches were restricted to the measurement of the heats of neutralization of tne following solutions :—

$$A = SO_3 + 200H_2O$$
$$B = HCl + 100H_2O$$
$$C = NaOH + 100H_2O$$
$$D = NH_4OH + 100H_2O$$

It was not thought necessary to extend these experiments to the determination of the heat of neutralization of potassium hydroxide, since all previous experiments have demonstrated the close agreement in behaviour of this substance with sodium hydroxide. I shall naturally omit the experimental details, and communicate only the numerical results. In the table below T represents the temperature of the experiment.

HEATS OF NEUTRALIZATION OF SULPHATES.

	T	$A + 2C$ Sodium sulphate.	T	$A + 2D$ Ammonium sulphate.
Temperature of experiment	9°·16 14°·42	32,059 c 31,646	9°·70 25°·26	28,459 c 29,541
Difference	15°·26	−413 c	15°·56	+1082 c

HEATS OF NEUTRALIZATION OF CHLORIDES.

	T	$B + C$ Sodium chloride.	T	$B + D$ Ammonium chloride.
Temperature of experiment	10°·14 24°·60	14,247 c 13,627	9°·60 24°·91	12,540 c 12,580
Difference	14°·46	−620 c	15°·31	+40 c

Thus at higher temperatures the heat of neutralization is smaller for sodium salts, but larger for ammonium salts. Now, if we put the change as proportional to the increase in temperature, which owing to the small temperature interval may be done without introducing any appreciable error, we shall then, by dividing the alteration in the heat of neutralization by the temperature interval, be able to determine the magnitude of the change for a rise of 1°. If we call the temperature coefficient ϕ, we obtain for the formation of

$$\text{Sodium sulphate } \phi = -\frac{413 \text{ c}}{15{\cdot}26} = -27 \text{ c}$$

$$\text{Ammonium sulphate } \phi = +\frac{1082}{15{\cdot}56} = +69$$

$$\text{Sodium chloride } \phi = -\frac{620}{14{\cdot}46} = -43$$

$$\text{Ammonium chloride } \phi = +\frac{40}{15{\cdot}31} = +2{\cdot}6$$

These values of ϕ are very different both in magnitude and in sign; but it will at once be seen that they stand in very close agreement with the specific heats of the initial and final solutions.

3. Dependence of the Thermal Effect upon the Specific Heats of the Solutions employed.

If the weights of the reacting solutions in the neutralization experiments (acid and base) be represented by A and B, and the specific heats of these two solutions and of the solution formed on neutralization $(A+B)$ by α, β, and γ, then the molecular heats of the three solutions will be

$$A \,.\, \alpha = q_a$$
$$B \,.\, \beta = q_b$$
$$(A + B)\gamma = q_c$$

Furthermore, the amount of heat which a solution of which the molecular heat is q will give up when it is cooled from a temperature of T to one of t is determined by the integral

$$\int_t^T q \,.\, dt.$$

Now, when the solutions A and B are at a temperature T, and the neutralization takes place at this temperature, then the solution formed $(A+B)$ must, when it is cooled to a temperature t, have a heat of neutralization R_T, and an amount of heat corresponding to the integral above will be evolved, so that the total heat effect is

$$R_T + \int_t^T q_c dt.$$

On the other hand, when both solutions A and B are first cooled from the temperature T to that of t before they act upon each other, then the mixed solutions, after having given rise to their heat of neutralization R_t, will also acquire the temperature t, and the total thermal effect will consequently be

$$\int_t^T (q_a + q_b) dt + R_t.$$

Now, since the initial and final states of the two substances A and B are the same in the two cases, the amount of heat produced must also be equal; so that we have

$$R_T - R_t = \int_t^T (q_a + q_b - q_c) dt \quad . \quad . \quad . \quad (1)$$

If now we regard the specific heats of the solutions as constant over the small temperature interval $T - t$, then the equation can be reduced to

$$R_T - R_t = (T - t)(q_a + q_b - q_c) \quad . \quad . \quad . \quad (2)$$

and the difference in the heat of neutralization for a rise of 1° *C. in temperature is*

$$\frac{R_T - R_t}{T - t} = q_a + q_b - q_c = \phi \quad . \quad . \quad . \quad (3)$$

This magnitude ϕ, which was determined above by direct neutralization experiments at different temperatures, can also be deduced from the specific heats of the solutions employed, or better still from their molecular heats. The solutions investigated had the following concentrations:—

$SO_3 + 200H_2O$
$HCl + 100H_2O$
$NaOH + 100H_2O$
$NH_4OH + 100H_2O$

If now, from the molecular heats contained in Table 16 on the specific heats of solutions, we calculate the value of ϕ, which, from what has been stated above, should be

$$\phi = q_a + q_b - q_c,$$

we obtain the following results for

SODIUM SULPHATE.

$A = 2NaOH + 200H_2O$ . . $q_a = 3562$ c
$B = SO_3 + 200H_2O$ . . . . $q_b = 3595$
$q_a + q_b = 7157$
$A + B = Na_2SO_4 + 401H_2O$ . . . $q_c = 7186$
$\phi = -29$ c

AMMONIUM SULPHATE.

$A = 2NH_4OH + 200H_2O$ . . $q_a = 3666$ c
$B = SO_3 + 200H_2O$ . . . . $q_b = 3595$
$q_a + q_b = 7261$
$A + B\ (NH_4)_2SO_4 + 401H_2O$ . . $q_c = 7196$
$\phi = +65$ c

SODIUM CHLORIDE.

$A = NaOH + 100H_2O$ . . . $q_a = 1781$ c
$B = HCl + 100H_2O$ . . . $q_b = 1770$
$q_a + q_b = 3551$
$A + B = NaCl + 201H_2O$ . . . $q_c = 3596$
$\phi = -45$ c

AMMONIUM CHLORIDE.

$A = NH_4OH + 100H_2O$ . . $q_a = 1833$ c
$B = HCl + 100H_2O$ . . . $q_b = 1770$
$q_a + q_b = 3603$
$A + B = NH_4Cl + 201H_2O$ . . . $q_c = 3606$
$\phi = -3$ c

A comparison of these values for ϕ, calculated from the specific heats of the solutions, with the results obtained from the direct neutralization experiments shows that there is complete agreement, and also proves the correctness of the equation

$$\frac{R_T - R_t}{T - t} = q_a + q_b - q_c = \phi.$$

The values are

Composition of the solution formed.	$\frac{R_T - R_t}{T - t}$	$q_a + q_b - q_c$
$Na_2SO_4 + 401H_2O$	−27 c	−29 c
$(NH_4)_2SO_4 + 401H_2O$	+69	+65
$NaCl + 201H_2O$	−43	−45
$NH_4Cl + 201H_2O$	+ 2·6	− 3

Hence it follows—

1. That the heats of neutralization of sodium sulphate and of sodium chloride *decrease* at higher temperatures;
2. That the heat of neutralization of ammonium sulphate *rises* with an increase of temperature, whilst that of ammonium chloride appears to be independent of the temperature; and
3. The change in the heat of neutralization with temperature is equal to the difference between the molecular heats of the original solution and of the solution formed, and is therefore equal to $q_a + q_b - q_c$; it is this number which is deduced from the specific heat of the liquid.

If now we assume that the specific heats of solutions do not change appreciably within a narrow range of temperature, we can put

$$R_t = R_o + \phi t \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and we find that the *dependence of the heat of neutralization upon the temperature* can be expressed by the figures given below, which apply to equivalent solutions of Na_2SO_4 and

$2NaCl$, etc. The concentration of all the reacting solutions was $R + 200H_2O$.

Composition of the solution formed.	Heat of neutralization at the temperature t.
$Na_2SO_4 + 401H_2O$	$32{,}306\ c - 27t\ c$
$2NaCl + 402H_2O$	$29{,}366 - 86t$
$(NH_4)_2SO_4 + 401H_2O$	$27{,}790 + 69t$
$2NH_4Cl + 402H_2O$	$25{,}030 + 5t$

In a similar manner the dependence of the heat of reaction upon the temperature can be calculated for other chemical processes.

4. Influence of Temperature upon the Heat of Solution of a Substance.

In an earlier chapter I have pointed out that the thermal effect due to the solution of a substance in water is dependent upon the amount of water used; but the temperature at which solution takes place has also, as has been explained above, an influence on the magnitude of the heat of solution.

Let L_T and L_t represent the heats of solution at temperatures T and t when 1 molecule of the substance dissolves in n molecules of water, and q and q_c represent respectively the molecular heats of the substance and of the solution formed; then, according to equation (3), we have approximately—

$$\phi = \frac{L_T - L_t}{T - t} = 18n + q - q_c$$

The change in thermal effect with rise of temperature can therefore be either positive or negative, according to whether $(18 + q)$ *is greater or less than* q_c. A few examples will now be brought forward.

The thermal effect on solution of *anhydrous salts* in water is either positive or negative; but for none of the salts that have hitherto been investigated is the molecular heat, q_c, of the solution formed greater than the sum of the molecular heats of the water and of the substance dissolved, $(18n + q)$;

ϕ will consequently be *positive for anhydrous salts*, and we can thus establish the following general rule :—

The thermal effect on solution of an anhydrous salt in water rises with the temperature of the water; that is to say, a negative heat of solution decreases in magnitude, whilst a positive heat of solution increases, when the temperature of the water is raised.

The thermal effect on solution of *hydrated salts* is partly positive, partly negative; but the molecular heat of the solution formed can be less as well as greater than the sum of the molecular heats of the constituents. This arises from the fact that the water in crystallized salts has a lower specific heat than the liquid water which is a constituent of the solution, and therefore, in this case, the relations will be more complicated. The heat of solution of magnesium sulphate will be taken as an illustration.

When a gram-molecule of $MgSO_4$ dissolves in n gram-molecules of water, and 1 gram-molecule of $MgSO_4 . 7H_2O$ dissolves in $(n - 7)$ gram-molecules of water, there is formed in both cases a solution of the same concentration, $MgSO_4 + nH_2O$. The change in thermal effect with temperature is in the two cases expressed by

For the anhydrous salt . . $\phi = 18 . n + q - q_c$
„ hydrated „ . . $\phi_1 = 18(n - 7) + q_1 - q_c$,

where q_c is the molecular heat of the solution formed, whilst q and q_1 represent respectively the molecular heats of the anhydrous and of the hydrated salts, which, according to the earlier investigations on the specific heats of these salts, are respectively 27 c and 100 c. Table 16 contains the values of q_c when n is equal to 20, 50, 100, and 200, and we therefore obtain

n	$MgSO_4$ $18n + q - q_c = \phi$	$MgSO_4 . 7H_2O$ $18(n - 7) + q_1 - q = \phi_1$
20	360 + 27 − 357 = 30	234 + 100 − 357 = − 23
50	900 + 27 − 874 = 53	774 + 100 − 874 = − 0
100	1800 + 27 − 1761 = 66	1674 + 100 − 1761 = + 13
200	3600 + 27 − 3541 = 86	3474 + 100 − 3541 = + 33

The heats of solution of the two salts at 18° and in 400 gram-molecules of H_2O are respectively +20,280 c and −3800 c. *But since ϕ and ϕ_1 rise with increase of temperature, so also will the change in the heats of solution of both salts rise with increasing amounts of water.* Furthermore, since ϕ is positive at all four dilutions, and the heat of solution of the anhydrous salt is positive, therefore the latter will also, in all cases, rise with an increase of temperature. For the crystallized salt with 7 molecules of water, of which the heat of solution is negative, the properties are different; for here a rise of temperature increases the negative thermal effect when the salt dissolves in 20 molecules of water; on the other hand, a smaller negative thermal effect is produced when the salt is dissolved in 100 or 200 molecules of water.

The change in thermal effect on solution of a substance with a rise of temperature is thus always dependent upon the difference between the molecular heats of the constituents and of the solution, or upon

$$q_a + q_b - q_c.$$

On solution of sulphuric acid, or on absorption of hydrogen chloride, in water the heat of solution rises with the temperature, and becomes still greater the larger the amount of water. According to Table 16, we have for

(H_2SO_4, nH_2O)

	$q_a + q_b - q_c = \phi$
when $n = 1$	$18 + 33 - 51 = 0$
„ $n = 5$	$90 + 33 - 108 = 15$
„ $n = 50$	$900 + 33 - 914 = 19$, etc.

Similarly for the absorption of hydrochloric acid in water.

(HCl, nH_2O)

	$q_a + q_b - q_c = \phi$
when $n = 10$	$180 + 7 - 162 = 25$
„ $n = 50$	$900 + 7 - 873 = 34$
„ $n = 100$	$1800 + 7 - 1170 = 37$, etc.

These examples will be sufficient to illustrate the influence of temperature upon the heat of solution of a substance.

5. Influence of Temperature upon the Thermal Effect on Dilution of Aqueous Solutions.

The experiments on the direct measurement of the heats of neutralization with variations of temperature, described in a preceding section, p. 167, are only a few examples chosen from a large number of experiments which I undertook during the winter of 1873 to 1874, with a view of determining the thermal effect of the same reaction when carried out at temperatures which differed widely from each other. In order to obtain reliable experimental results, it was necessary that the laboratory should be at the same temperature as the liquid in the calorimeter, and I therefore limited the experiments to a difference of temperature of from 16° to 18°, since I worked partly at 7° to 8°, partly at 25° to 26° C., the last-mentioned temperature being unpleasantly hot for prolonged researches.

The whole of this work was in a way unnecessary, since, as I have already shown, the values sought can be calculated from the specific heats of the liquids employed; but this method does not lead to such accurate results as the determination of the thermal effect of reactions in aqueous solutions, and, besides, I always prefer to have direct confirmation of theoretical deductions.

The researches include the relations between sulphuric acid, hydrochloric acid, and caustic soda, together with their salts, in aqueous solution, and deal partly with the *thermal effect on neutralization*, partly with the *dilution of solutions*, and finally with *partial decomposition*. All three phenomena were studied at different temperatures and at different degrees of dilution.

Numerical results upon the influence of temperature on the heat of dilution of solutions are given below (see *Therm. Unters.*, i. pp. 80–88), where each result given is the mean value of three separate experiments.

SULPHURIC ACID SOLUTION AND WATER.

$(H_2SO_4 . nH_2O, nH_2O)$			
$n =$	50	100	200
T	25·26°	25·04°	24·92°
t	8·05	8·07	8·00
R_T	206 c	244 c	324 c
R	99	150	228
$R^T - R_t$	107 c	94 c	96 c
$T - t$	17·2°	17·0°	15·9°
$\phi = \frac{R_T - R_t}{T - t}$	6·2	5·5	5·7

As before, ϕ represents the change in thermal effect for a rise of 1° C. in temperature. The thermal effect at 0° is then found from the following equation :—

$$R_o = R_t - \phi t;$$

for the three degrees of dilution we therefore have the following expression for the heat of dilution :—

$$\begin{aligned} \text{for } n = 50 \quad & R_t = 50 \text{ c} + 6{\cdot}2t \\ n = 100 \quad & R_t = 106 + 5{\cdot}5t \\ n = 200 \quad & R_t = 183 + 5{\cdot}7t \end{aligned}$$

For the remainder of the reactions the investigations were carried out in a similar manner, and I shall therefore limit myself to a statement of the conclusions arrived at, and refer the reader to my earlier work for further details.

TABLE 17.

INFLUENCE OF TEMPERATURE UPON THE HEAT OF DILUTION

Reaction.	n	Thermal effect at $t°$.
$(H_2SO_4 . nH_2O, nH_2O)$	50	$50 + 6{\cdot}2t$
	100	$106 + 5{\cdot}5t$
	200	$183 + 5{\cdot}7t$
$(2HCl . (n+1)H_2O, nH_2O)$	50	$322 + 6{\cdot}6t$
	100	$74 + 8{\cdot}7t$
	200	$-22 + 10{\cdot}2t$
$(2NaOH . nH_2O, nH_2O)$	50	$-687 + 21t$
	100	$-540 + 17t$
	200	$-396 + 15t$
$(Na_2SO_4 . (n+1)H_2O, nH_2O)$	100	$-845 + 21t$
	200	$-593 + 19t$
	400	$-396 + 17t$
$(2NaCl . (n+1)H_2O, nH_2O)$	100	$-495 + 12{\cdot}5t$
	200	$-332 + 12{\cdot}0t$
$(Na_2SO_4 . 2HCl . nH_2O, nH_2O)$	150	$-205 + 15{\cdot}5t$
$(2NaCl . H_2SO_4 . nH_2O, nH_2O)$	300	$-62 + 14{\cdot}5t$
	300	

The preceding table thus contains the results of my researches on the influence of temperature upon the thermal effect on dilution of aqueous solutions at different concentrations. In every case the solution was diluted with an amount of water equal to that which it already contained; that is to say, the concentration was halved in each successive experiment. The thermal effect is expressed in the table as the sum of the thermal effect at 0° and of the heat-change which takes place when the temperature rises t degrees.

I have measured the thermal effect of sodium chloride at 25° for dilutions other than the above-mentioned, and have found

for $n =$	25	50	100	200	400
$R_{25} =$	-408 c,	-331 c,	-186 c,	-43 c,	$+6$ c.

For two only of these dilutions (100 and 200) was it possible to carry out a measurement at about 7°, since, owing to the mildness of the winter, the temperature of the air was usually above 7°.

A glance at the numbers contained in the last column of the table leads to the following general conclusion :—

The change in thermal effect which occurs with a rise of temperature is always positive, quite independently of whether the thermal effect on dilution of an aqueous solution with water be positive or negative.

For solutions of sulphuric and hydrochloric acids the thermal effect is positive, for the other substances investigated it is negative; but the change with rise of temperature is always positive.

This general result could also be deduced from my determinations of the specific heats of aqueous solutions, from which it is evident that the *molecular heat of an aqueous solution when mixed with water is always less than the sum of the molecular heats of the original solution and of the water used in dilution.* If q_a, q_b, q_c represent these three values, the change in thermal effect with a rise of temperature will be

$$\phi = \frac{d \cdot R}{dt} = q_a + q_b - q_c > 0,$$

as has been shown by direct experiment; but in this manner ϕ can be determined with far greater accuracy than when the value is deduced from the specific heats of the solutions.

6. Influence of Temperature and of Dilution upon the Thermal Effect of Partial Decomposition in Aqueous Solutions, and upon the Degree of Dilution.

In Chapter V. I have recorded the results of my researches on the partial decomposition which takes place when an acid acts upon a salt in aqueous solution. Fundamental experiments have shown that when equivalent quantities of nitric acid and sodium sulphate react upon each other in aqueous solution, the base is distributed between the two acids in the ratio of 2 : 1, so that two-thirds of the base is united to nitric acid and only one-third to sulphuric acid. A precisely similar ratio holds when hydrochloric acid replaces nitric in the reaction mentioned.

The ability of an acid to obtain possession of a base I have called the *avidity* of the acid, and have chosen nitric and hydrochloric acids as the unit. The avidity of sulphuric acid will then be 0·5. The avidity of many other acids with respect to sodium hydroxide, as well as the relative avidities of sulphuric and hydrochloric acids for certain other bases, follow from the researches already described.

These values, however, only hold good when the conditions of the corresponding experiments are exactly fulfilled; that is to say, when the concentration of the solution, and its temperature, are the same as those of the original experiment.

It still remains to be determined *how far the degree of partial decomposition will be influenced by the concentration of the solution and by the temperature of the experiment.* This problem forms the subject of the following investigation.

The experiments now to be described conclude the calorimetric determinations (160 in all) which I undertook during the winter of 1873 to 1874, partly at a temperature of about 7°, partly at about 25°. Besides the fundamental experiments on partial decomposition, there are also included experiments on the relations between sulphuric acid, hydrochloric acid, and caustic soda. Three different degrees of dilution were employed, at each of which measurements of the thermal effect were carried out by six different processes, and this was done both at the high and at the low temperature. No less than thirty thermal measurements were therefore made for each substance, and in every case two or three separate determinations were carried out.

The five reactions take place between—

1. Sodium sulphate and an equivalent amount of hydrochloric acid;
2. Sodium chloride and an equivalent amount of sulphuric acid;
3. Sodium sulphate with twice the equivalent amount of sulphuric acid;
4. Sodium chloride with half an equivalent of hydrochloric acid; and
5. Finally, the thermal effect due to the mixing of the two

liquids formed in 3 and 4 should be measured; the liquids so formed will have the same composition as the liquids resulting from 1 and 2.

For the sake of brevity the solutions employed will be represented by P, Q, and B, so that

$$P = H_2SO_4 + nH_2O$$
$$Q = 2HCl + nH_2O$$
$$B = 2NaOH + (n - 1)H_2O$$
$$BP = Na_2SO_4 + (2n + 1)H_2O$$
$$BQ = 2NaCl + (2n + 1)H_2O$$

For the three degrees of dilution n equalled respectively 50, 100, and 200.

Results of the experiments at a dilution $n = 50$ are compared in the next table.

Reaction $n = 50$	Thermal effect at about 7·4°	Thermal effect at about 25°	$R_o + \phi t$
(BP, Q)	−2916 c	−3823 c	−2535 c − 51·5t
(BQ, P)	+ 453	+ 391	+ 481 − 3·6t
$(B, Q) - (B, P)$	−3369 c	−4214 c	−3016 c − 47·9t
$(BP, 2P)$	−2262 c	−3154 c	−1879 c − 51·0t
$(2BQ, Q)$	+ 325	+ 262	+ 352 − 3·7t
(BP_3, B_2Q_3)	− 66	− 165	− 24 − 5·6t
Sum S	−2003 c	−3057 c	−1551 c − 60·3t

The first line contains the thermal effect of the reaction of $Na_2SO_4 . 50H_2O$ upon $2HCl . 50H_2O$, both at 7·4° and at 25°, whilst the last column in the same line gives the calculated heat of reaction at 0° and the temperature coefficient ϕ. The second line contains the thermal effect of the reverse reaction—that is, between $H_2SO_4 . 50H_2O$ and $2NaCl . 50H_2O$. The difference between the numbers in the two lines will, as was pointed out on p. 144, be equal to the difference between the heats of neutralization of hydrochloric and sulphuric acids.

Now, if the bases in these two reactions are distributed between hydrochloric and sulphuric acids in the ratio 2 : 1,

then both the liquids formed will contain the substances in the following proportions:—

$$\tfrac{2}{3}BQ + \tfrac{1}{3}BP + \tfrac{1}{3}Q + \tfrac{2}{3}P, \text{ or}$$
$$\tfrac{1}{3}(2BQ + BP + Q + 2P),$$

and the following reaction will take place, namely—

$$\tfrac{1}{3}[(BP, 2P) + (2BQ, Q) + (BP_3, B_2Q_3)] = \tfrac{1}{3}S.$$

The thermal effects of these three reactions are given in lines 4, 5, and 6.

The total thermal effect in the reaction (BP, Q), in which two-thirds of a molecule of Na_2SO_4 are decomposed and two-thirds of 2NaCl are formed, must therefore be

$$(BP, Q) = -\tfrac{2}{3}\cdot 3369 \text{ c} - \tfrac{1}{3}\cdot 2003 \text{ c} = -2914 \text{ c at } 7{\cdot}4^\circ$$
$$= -\tfrac{2}{3}\cdot 4214 \text{ c} - \tfrac{1}{3}\cdot 3057 \text{ c} = -3828 \text{ c at } 25^\circ$$

The complete agreement between these numbers, namely, -2914 c and -3828 c, with those found directly for the reaction (BP, Q), that is -2916 c and -3828 c, proves that the assumption made in the calculation, namely, that the base is divided between the two acids in the ratio 2 : 1, is entirely justified, and it therefore follows *that the temperature does not exercise any influence upon the degree of partial decomposition at the dilution employed.*

The next group of experiments gives the thermal effects of the same reactions in solutions containing double the amount of water, $n = 100$.

Reaction $n = 100$	Thermal effect at about 7·4°	Thermal effect at about 25°	$R_0 + \phi t$
(BP, Q)	-2775 c.	-3744 c	-2380 c $-53{\cdot}8\,t$
(BQ, P)	$+669$	$+576$	$+707 - 5{\cdot}2\,t$
$(B, Q)-(B, P)$	-3444 c	-4320	-3087 c $-48{\cdot}6\,t$
$(BP, 2P)$	-1800 c	-2664 c	-1434 c $-49{\cdot}2\,t$
$(2BQ, Q)$	$+140$	$+135$	$+142 - 0{\cdot}3\,t$
(BP_3, B_2Q_3)	$+114$	$+64$	$+137 - 3{\cdot}0\,t$
Sum S	-1546 c	-2465 c	-1155 c $-52{\cdot}5\,t$

Assuming that the degree of partial decomposition is the same as at the dilution $n = 50$, we obtain for (BP, Q) the following calculated values :—

$$(BP, Q) = \begin{cases} -\frac{2}{3} \quad 3444\,c - \frac{1}{3} \times 1546\,c = -2811\,c \text{ at about } 7{\cdot}4^\circ \\ -\frac{2}{3} \times 4320\,c - \frac{1}{3} \times 2465\,c = -3702\,c \text{ at about } 25^\circ \end{cases}$$

The small difference between the calculated values for (BP, Q) and those determined by direct experiment, namely, $+36$ and -42 c, which amounts to only about 1 per cent. of the heat of neutralization, shows that the *degree of decomposition is also at this dilution practically independent of the temperature.*

Experiments at the *third* degree of dilution ($n = 200$) showed that, owing to the great dilution, it is not possible to obtain accurate measurements of the thermal effect in the case of reactions 4 and 5. It was therefore necessary to adopt some other method in order to confirm the statement that a base in the presence of equivalent amounts of different acids will always be distributed between them in an invariable ratio.

When a solution contains equivalent quantities of sodium hydroxide, sulphuric acid, and hydrochloric acid, and the partition-coefficient is as 1 : 2, then the solution will have the composition $B\frac{1}{3}P + B\frac{2}{3}Q$, employing the same signs as before. If now we mix these two solutions, the one containing $B\frac{1}{3}P$ and the other $B\frac{2}{3}Q$, then no reaction should take place, provided the partition-coefficient had been correctly determined, and, as a natural consequence, there will not be any appreciable thermal effect.

Solutions were therefore prepared of the composition B_nP and $B_{1-n}Q$, where n represents successively $\frac{2}{7}$, $\frac{1}{3}$, $\frac{2}{5}$, and $\frac{1}{2}$. On mixing two such solutions it is easy to calculate from the observed thermal effect what the partition-coefficient must be in order to obtain a zero or minimum value for the thermal effect. Experiments were carried out at 18°, and with solutions of two degrees of dilution, such that after mixing they contained respectively 150 and 300 equivalents of water for 1 equivalent of the base. The result was as follows :—

$(B_nP, B_{1-n}Q)$

n	$1-n$	150 mol. H_2O	300 mol. H_2O	$n:(1-n)$
$\frac{2}{7}$	$\frac{5}{7}$	+ 57 c	+229 c	2 : 5
$\frac{1}{3}$	$\frac{2}{3}$	− 41	+ 28	1 : 2
$\frac{2}{5}$	$\frac{3}{5}$	−185	−128	2 : 3
$\frac{1}{2}$	$\frac{1}{2}$	−576	−550	1 : 1

From this it is evident that the thermal effect is at its lowest value when the base is distributed between the acids in the ratio 1 : 2.

Summing up all the data available, we may undoubtedly arrive at the following conclusions :—

1. *When* 1 *equivalent of sulphuric acid,* 1 *equivalent of hydrochloric acid* (*or* 1 *equivalent of nitric acid*), *and* 1 *equivalent of caustic soda react upon each other in aqueous solution, the base is distributed between the two acids in the ratio* 1 : 2.
2. *The partition-coefficient does not change, either with the amount of water in the solution, or with its temperature, to such an extent that any alteration can be detected with certainty by calorimetric measurements.*

The magnitude of the avidity must therefore be regarded as a characteristic value for each acid, and this is the case also with regard to its influence on other reactions. The observations of Mills and Hogarth (*Proc. Roy. Soc.*, 28, 270) are therefore not without interest, since they prove that cane sugar is inverted into glucose and levulose with equal rapidity by molecular quantities of hydrochloric or of sulphuric acid (either by HCl or by H_2SO_4); that is to say, the influence of equal equivalents are as 2 : 1.

The outcome of the researches on the influence of temperature on the thermal effect of chemical reactions in aqueous solutions, as, for instance, neutralization, solution in water, dilution of aqueous solutions, and partial decomposition of salts by acids, is therefore to show that *temperature exercises*

an appreciable influence on the magnitude of the thermal effect in the individual cases; but it is also apparent that these influences are closely connected with the specific heats of the solutions employed, from which they can be theoretically calculated (see p. 169).

PART II

COMPOUNDS OF NON-METALS

CHAPTER VIII

COMPOUNDS OF THE NON-METALS—METHODS OF INVESTIGATION AND THEORETICAL RESULTS

The thermal effect which accompanies the formation of a chemical compound from its elements is, as is well known, equal to the difference between the total energy of the constituents and that of the compound formed, and is consequently a partial expression of the mutual affinities of the elements; for when a compound is again resolved into its elements an equal amount of energy must be supplied to that which is given up on formation of the compound. The relation between the magnitude of the affinity and that of the thermal effect is, however, rather more complex. Elements, like compounds, are aggregates of atoms, but with this difference—that whilst the molecule of an element is composed of similar atoms, that of a compound is composed of dissimilar atoms. *Reactions between elements are therefore of precisely the same character as reactions between compounds;* in both cases the original molecules are decomposed and new molecules are formed. The thermal effect accompanying the reactions will, therefore, under similar conditions, depend upon the difference between the total energy of the molecules decomposed and that of the molecules formed.

When chlorine unites with hydrogen there is no change in the state of aggregation, since both of the constituents as well as

the compound formed are gaseous, neither is there any change in volume. The reaction between nitrogen and oxygen to form nitric oxide (NO) is equally simple; all the substances concerned are gaseous, and there is no change of volume. The thermal effect in these examples may, therefore, bear a simple relation to the affinities between them. But experiments show that the thermal effect for a molecule of the reacting elements is in the first case +44,000 c, in the second case −43,150 c.

Now, if the molecules of the gaseous elements be supposed to be built up in the simplest manner, so that each molecule contains two atoms, the reactions referred to can be expressed as follows:—

$$(H_2 : Cl_2) = 2(H, Cl) - (H, H) - (Cl, Cl) = +44{,}000 \text{ c}$$
$$(N_2 : O_2) = 2(N, O) - (N, N) - (O, O) = -43{,}150$$

Whence it follows that

$$(H, Cl) = 22{,}000 \text{ c} + \tfrac{1}{2}(H, H) + \tfrac{1}{2}(Cl, Cl)$$
$$(N, O) = -21{,}575 \text{ c} + \tfrac{1}{2}(N, N) + \tfrac{1}{2}(O, O);$$

that is to say, the affinity between chlorine and hydrogen must be greater than 22,000 c, provided that the formation of the molecules of these elements from their atoms is accompanied by an evolution of heat; or, in other words, provided the atoms of the elements are joined together by positive affinities.

Now, it is not likely that similar atoms would unite to form molecules unless there were a mutual attraction between them, and *the decomposition of the molecule of an element into its atoms must therefore be accompanied by a loss of energy.*

If, then, the formation of the molecule NO gives rise to a negative thermal effect, it must be because the decomposition of the original molecules of nitrogen and oxygen absorbs a greater amount of energy than corresponds to the formation of the molecule of NO from the atoms of nitrogen and oxygen in the free state. *The more strongly the atoms of an element are bound together within the molecule the greater will be the difficulty in decomposing such a molecule, and the smaller will be the tendency*

of the element to react with other substances. It is precisely this property which appears to be characteristic of nitrogen.

From the preceding examples it is evident that *the thermal effect which is observed in what is known as direct synthesis is not an absolute measure of the affinity of the constituents of the compound formed.* But a measure of the heats of formation of compounds is, nevertheless, of great importance as a means by which we may arrive at some knowledge of the true affinities of the elements. We shall refer later to an experiment dealing with this question.

The heat of formation of a compound can be measured either directly or indirectly. The first method gives results which are independent of any other determinations, and will consequently lead to the most accurate results, provided always that the direct formation takes place under conditions favourable to an exact calorimetric measurement of the resulting thermal effect. This result is, however, attained only for a very small number of compounds, such as water, hydrogen chloride, carbon dioxide, sulphur dioxide; but in most cases the direct union of elements takes place only at a higher temperature than is compatible with accurate calorimetric work.

In the majority of cases, therefore, we are obliged to determine the required thermal effect in an *indirect* manner, by means of single or double decomposition in *aqueous solution.* As a rule this method also gives very trustworthy results when the fundamental numbers employed in the calculations have been determined with sufficient care. *But the heat of formation of certain compounds must be directly measured in every case,* and fortunately this can be done for many of the substances which most frequently form the basis of the calculations. Special care was therefore devoted to measuring the thermal change on formation of water, hydrogen chloride, sulphur dioxide, carbon monoxide, chlorine monoxide, and other equally important compounds.

In the present chapter we shall give an account of the special methods which were adopted in determining the heats of formation of compounds of the non-metals. The subject-matter is divided into four main groups, namely—

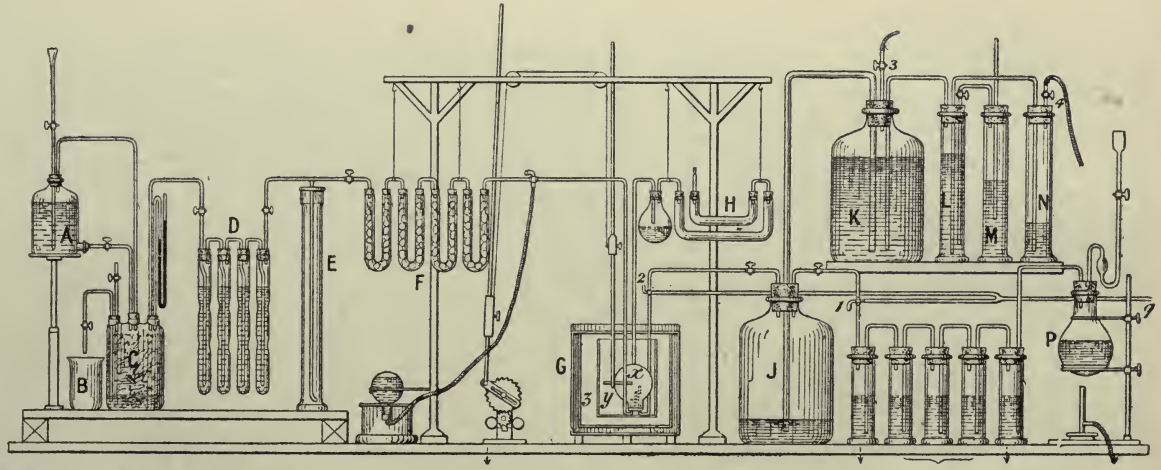
A. Hydrogen compounds of the non-metals,
B. Oxygen " " "
C. Chlorine " " "
D. Sulphur and nitrogen compounds of carbon,

and in each of the groups the substances are arranged in order of the valency of the non-metals; as, for instance, chlorine, bromine, and iodine; oxygen, sulphur, selenium, and tellurium, etc. After all the compounds have been described in this manner, the numerical results obtained will be tabulated in Chapter IX. For complete experimental details the reader is referred to *Therm. Unters.*, vol. ii.

A. Hydrogen Compounds of the Non-metals.

1. Hydrogen Chloride, Hydrogen Bromide, and Hydrogen Iodide.

The heat of formation of *hydrogen chloride* is measured *directly* by burning dry chlorine in an atmosphere of hydrogen; whilst in the case of *hydrogen bromide*, and in that of *hydrogen iodide*, the thermal effect is derived from the decomposition of an aqueous solution of the bromide and iodide of potassium by means of dry gaseous chlorine. In addition, the thermal effect due to the absorption in water of these three gaseous hydrogen halides, and also of chlorine, as well as the heat of solution of bromine in water, were determined, and finally the latent heat of bromine was measured at 17°. The results are compared in the table below. All particulars will be found in *Therm. Unters.*, vol. ii. pp. 8–43; here I shall only mention that in the first group of experiments 33 litres of hydrogen chloride were formed by burning chlorine in hydrogen, and that the latent heat of bromine was determined by evaporating 19 grams of bromine in a calorimeter by means of a current of air at 17° C. A diagram of the apparatus used has, however, been reproduced (see Fig. 8).



A, B, C, D, E, F. Apparatus for generating and purifying hydrogen. For details, see Fig. 7.

Motor for driving stirring apparatus.

G. Calorimeter consisting of { *x*. Platinum bulb, 500 c.c. capacity. *y*. Vessel containing 3000 gr. water. *z*. Double-walled outer vessel.

H. Flask and tubes containing distilled water for absorption of HCl formed in *x*.

Con. H_2SO_4. Water. Con. HCl

J, K. Gas-holders of 8-litre capacity for storing chlorine over con. H_2SO_4.

L, M, N. Gas-bottles containing con. H_2SO_4 for regulating the flow of gas.

P. Flask for generating chlorine.

q. Tube leading outside the room for escape of chlorine.

1. Three-way tap in connection with *q*.

2. Three-way tap in connection with *q* and *x*.

3 and 4. Taps in connection with aspirators.

FIG. 8.—Apparatus for measuring the heat of formation of hydrogen chloride, etc.

R	(R, H)	(RH, Aq)	(R, H, Aq)
Cl Gas	22,001 c	17,314 c	39,315 c
Br Liquid	8,440	19,936	28,376
I Solid	−6,036	19,207	13,171

$(Cl_2, Aq) = 4870$ c heat of absorption
$(Br_2, Aq) = 1078$ „ solution
Br_2 gas $- Br_2$ liquid $= 6563$ „ vaporization.

The *second* column shows that the thermal effect on formation of these gaseous compounds is greatest for hydrogen chloride, very much less for hydrogen bromide, and becomes negative for hydrogen iodide. This behaviour is exactly parallel with the stability of these same compounds with a rise of temperature; for whilst hydrogen chloride is decomposed only at a very high temperature, the dissociation of hydrogen bromide takes place on feeble heating, and hydrogen iodide decomposes spontaneously at ordinary temperatures.

The *third* column contains the *heats of absorption* of the substances; and it is noteworthy that hydrogen chloride has a lower value than the other two, which are of almost equal magnitude; this is not due to any error of experiment, since the fact has been confirmed in other determinations.

In the *fourth* column are included the sums of the numbers contained in the second and third columns; that is to say, the thermal effect on formation of aqueous solutions of these substances from their elements. These numbers serve to exemplify the different degrees of affinity of the halogens, which are also shown by the well-known fact that chlorine can decompose both hydrogen bromide and hydrogen iodide in aqueous solution (as well as in the free state), and that bromine can decompose hydrogen iodide, whilst iodine does not exercise any influence on the two other hydrogen halides.

The unequal affinities are also apparent in the behaviour of these solutions towards oxygen (or atmospheric air); since an aqueous solution of hydrogen chloride, as is well known, is not decomposed on long exposure to the air, whilst aqueous

hydrogen bromide is very soon coloured yellow by partial oxidation, and aqueous hydrogen iodide is gradually completely decomposed by atmospheric oxygen.

Then again, the unequal affinity is shown by the fact that chlorine and hydrogen unite together very readily, bromine and hydrogen require the aid of a rise of temperature, and then only unite partially, whilst the rate of union of iodine with hydrogen is still slower.

The heats of formation given for the three compounds can, however, only be compared with certain limitations; for chlorine is a gas, bromine a liquid, and iodine a solid body. If the thermal effect refers to the three substances in the gaseous state, and at the same temperature, then the heats of vaporization of bromine and iodine must be added on. For half a gram-molecule of bromine this has been shown above to be 3281 c; for half a gram-molecule of iodine calculations from earlier experiments give a value of 5448 c, if the formation of hydrogen iodide be supposed to take place at 19° C. We then have

$$\left.\begin{array}{l}\text{for bromine vapour } (H, Br_{gas}) = 8440\,c + 3281\,c = 11{,}721\,c \\ \text{for iodine vapour } (H, I_{gas}) = -6036 + 5448 = -588\end{array}\right\} \text{at } 19°.$$

Since the thermal effect is dependent upon the temperature (see Chapter VII.), and the variation between the temperature limits of T and t are represented by the equation

$$R_T - R_t = (T-t)(q_a + q_b - q_c),$$

where q_a and q_b are the molecular heats of the elements, and q_c that of the compound, the difference in the preceding case being 0·9 c, then the thermal effect at 0° can be found by deducting $19 \times 0{\cdot}9$ c from the number above. We thus obtain

$(H, Cl) = 21{,}984 + 0{\cdot}9t$	Valid at the temperature t when all the constituents are assumed to be in the gaseous state.
$(H, Br_{gas}) = 11{,}704 + 0{\cdot}9t$	
$(H, I_{gas}) = -605 + 0{\cdot}9t$	

At the boiling-point of iodine the heat of formation of hydrogen iodide will therefore be -605 c $+ 180 \times 0{\cdot}9$ c $= -443$ c.

2. Water, Hydrogen Peroxide, and Hydrogen Sulphide.

(*a*) The heat of formation of *water*—that is to say, the heat of combustion of hydrogen—is measured *directly* by burning oxygen in hydrogen, and in the seven experiments carried out 18·93 grams of water were formed. The result, calculated for 18 grams of water, is

$$(H_2, O) = 68{,}357 \text{ c},$$

where the product of combustion is liquid water at 18° C. If, in accordance with more recent determinations, we call the molecular weight of water 18·015, then the molecular heat of combustion becomes 68,414 c, or 0·8 per cent. greater. But in calculating the results of all the later experiments into which the heat of combustion of hydrogen enters the number 68,360 c was always used, and since the required correction is so very small, namely, 1·0008 times the value employed, I have not thought it necessary to alter all the derived numbers.

The heat of formation is necessarily influenced by the temperature and state of aggregation of the water resulting from the combustion. If, after combustion has taken place, we assume the water present as vapour at 18°, then the heat of combustion will be 10,424 c lower (owing to the latent heat of water), and if the variation with temperature be estimated in the manner previously described (p. 170), we arrive at the following general results:—

(α) *The thermal effect on formation of* 1 *gram-molecule of water from oxygen and hydrogen at constant pressure and temperature t amounts to*

$$68{,}496 \text{ c} - 7{\cdot}7^\circ\, t, \text{ Product liquid,}$$

when liquid water at the temperature t is formed;

(β) *The thermal effect on formation of* 1 *gram-molecule of water from oxygen and hydrogen at constant pressure and temperature t amounts to*

$$57{,}904 \text{ c} + 1{\cdot}65^\circ t, \text{ Product gaseous,}$$

when water vapour is formed at the temperature t.

(*b*) The heat of formation of *hydrogen peroxide* was determined by measuring the thermal effect of its reduction in aqueous solution by means of stannous chloride. The reaction is very vigorous, and is accompanied by a thermal effect of 88,820 c for each gram-molecule of hydrogen peroxide. Thus we find that hydrogen peroxide loses one of its atoms of oxygen and is converted into water with a *heat-evolution* of 23,059 c per gram-molecule, and that consequently the thermal effect on formation of hydrogen peroxide by the oxidation of water must be negative, namely—

$$(H_2O, O, Aq) = -23{,}059 \text{ c.}$$

This negative character explains, on the one hand, why it is that water cannot be directly oxidized to hydrogen peroxide by means of free oxygen, and, on the other, why an aqueous solution of the peroxide is so easily decomposed, since the decomposition is attended by a considerable evolution of heat; hydrogen peroxide therefore acts as a very strong oxidizing agent.

If we add the heat of formation of water, namely 68,357 c, to the preceding number we obtain the *heat of formation of* 1 *gram-molecule of hydrogen peroxide in aqueous solution.*

$$(H_2, O) + (H_2O, O, Aq) = (H_2, O_2, Aq) = +45{,}298 \text{ c.}$$

(*c*) *Hydrogen sulphide.*—Sulphur occurs in several allotropic modifications, which differ amongst themselves in the amount of energy they contain; whence it follows that the conversion from one state into the other is accompanied by a thermal change.

It is therefore of the utmost importance, in comparing the heats of formation of the different compounds of sulphur, that we should always start with the sulphur in the same condition. Amongst the various allotropic modifications the *rhombic* undoubtedly appears to be the stable form, and it is, moreover, the one in which the sulphur can most easily be obtained, and with always the same properties. I have consequently chosen rhombic sulphur as the starting-point for my measurements. By burning sulphur in oxygen the *heat of formation of sulphur dioxide can be determined directly*, and the burning of hydrogen

sulphide in oxygen provides us with material for an *indirect determination of the heat of formation of hydrogen sulphide.* It is, of course, necessary in these determinations to allow for the small amount of the trioxide which is always formed when sulphur is burned. The experiments which were undertaken for the estimation of the heat of combustion of hydrogen sulphide are described in detail in *Therm. Unters.*, vol. iv. pp. 184–189. There we find that the heat of combustion of 1 gram-molecule of H_2S amounts to 136,710 c. This magnitude is naturally equal to the difference between the heats of combustion of the elements and the heat of formation of hydrogen sulphide, so that

$$(H_2, O) + (S, O_2) - (H_2, S) = 136{,}710 \text{ c.}$$

For the heat of formation of sulphur dioxide from rhombic sulphur I have found 71,080 c (see below), and the heat of combustion of hydrogen has already been given as 68,360 c; from which it follows that

$$(H_2, S) = 2730 \text{ c}$$

is the heat of formation of 1 gram-molecule of hydrogen sulphide from rhombic sulphur.

Ten years ago I had attempted to determine this magnitude by the action of hydrogen sulphide upon an aqueous solution of iodine in hydriodic acid; sulphur and hydriodic acid were hereby formed; but the sulphur was precipitated in a *soft, amorphous condition*, and the calculation led to a heat of formation of 4740 c for 1 gram-molecule of hydrogen sulphide. This is of interest, inasmuch as it gives us the magnitude of the thermal effect corresponding to the conversion of amorphous into crystalline, rhombic sulphur; for the latter will be the difference between the values 4740 c and 2730 c, or 2010 c for every 32 grams of sulphur.

The thermal effect due to the *absorption* of hydrogen sulphide in water was found by direct measurement to be

$$(H_2S, Aq) = 4560 \text{ c,}$$

from which it follows that

$$(H_2, S, Aq) = 7290 \text{ c.}$$

(*d*) *A comparison between the heats of formation of hydrogen chloride and of hydrogen iodide with those of water and of hydrogen sulphide shows the following interesting relation :—*

$(H_2, Cl_2, Aq) = 78{,}630$ c	$(H_2, Cl_2) = 44{,}148$ c	at 100°
$(H_2, O, Aq) = 68{,}360$	$(H_2, O) = 58{,}063$	
Difference + 10,270	Difference − 13,915 c	

or in words: In aqueous solution chlorine has a greater affinity for hydrogen than has an equivalent amount of oxygen; chlorine, therefore, in aqueous solution, will decompose water. *Conversely*, oxygen will decompose dry hydrogen chloride at 100° with the formation of free chlorine and water vapour; this property is the basis of what is known as the *Deacon* process for the preparation of free chlorine from hydrogen chloride and atmospheric air. Both processes take place with a large evolution of heat.

A precisely similar relation holds between hydrogen iodide and hydrogen sulphide, namely—

$(H_2, I_2, Aq) = 26{,}342$ c	$(H_2, I_2) = -12{,}072$ c
$(H_2, S, Aq) = 7{,}290$	$(H_2, S) = +2{,}730$
Difference + 19,052 c	Difference − 14,802 c

or in words: In aqueous solution iodine has a stronger affinity for hydrogen than has sulphur; consequently, iodine will decompose an aqueous solution of hydrogen sulphide; but the *reverse* process is known to occur when there is no water present, for then gaseous hydrogen iodide is decomposed by sulphur with the formation of free iodine and hydrogen sulphide. Both processes are attended by an evolution of heat.

These examples also show how the *chemical action between two substances can change completely in character according to whether the reaction takes place in aqueous solution or between the substances in the dry state.*

3. Ammonia and Hydroxylamine.

(*a*) *Ammonia.*—The heat of formation of this compound is derived from a knowledge of the thermal effect due to the combustion of dry ammonia gas in oxygen, and of the weight of

water formed therefrom. In eight experiments there were formed in all 34·35 grams of water, corresponding to the combustion of approximately 28 litres of gaseous ammonia. The heat of combustion per gram-molecule of ammonia was equal to 90,648 c, and in calculating the results of the experiments it was, of course, necessary to take into account the small amount of nitric acid always formed in the combustion. By the combustion of 1 gram-molecule of NH_3 $\frac{3}{2}$ gram-molecules of water are formed, and the process may be expressed as

$$(NH_3, \tfrac{3}{2}O) = 90{,}648\text{ c} = \tfrac{3}{2}(H_2, O) - (N, H_3);$$

but since the heat of combustion of hydrogen, as has been previously stated, amounts to 68,360 c per gram-molecule, the heat of formation of ammonia will be

$$(N, H_3) = 11{,}890\text{ c.}$$

The heat of *absorption* of 1 gram-molecule of ammonia gas in approximately 200 gram-molecules of water has been found to be

$$(NH_3, Aq) = 8435\text{ c,}$$

from which we obtain for the formation of ammonia in aqueous solution

$$(N, H_3, Aq) = 20{,}325\text{ c.}$$

(*b*) *Hydroxylamine.*—In the course of investigating the behaviour of hydroxylamine towards oxidizing agents in aqueous solution I resolved to carry out oxidation experiments with silver oxide, which not only acts quickly but also gives constant results. The products of the reaction were carefully examined, and it was found that *hydroxylamine on oxidation with silver oxide* gives rise to nitrogen, nitrous oxide, and water, in the following proportions :—

$$4NH_3O + O_3 = N_2 + N_2O + 6H_2O.$$

The oxidation was carried out in such a manner that an aqueous solution containing 2 molecules of hydroxylamine nitrate ($NH_3O.HNO_3$) and 3 molecules of silver nitrate were mixed with an aqueous solution of ammonia, so that after the reaction the liquid contained one-sixth of the total amount of

ammonia in the free state, the remainder being in combination with the nitric acid. The reaction takes place immediately after mixing the two liquids in the calorimeter, and is completed in the course of a few seconds. From the observed thermal effect, namely, 82,608 c for each gram-molecule of hydroxylamine, we can calculate the heat of formation of hydroxylamine in aqueous solution, thus—

$$(N, H_3, O, Aq) = 24{,}290 \text{ c.}$$

At the same time I also determined the *heat of neutralization;* which for 2 gram-molecules of hydroxylamine amounts to 21,580, 18,520, and 18,840 c respectively for sulphuric, hydrochloric, and nitric acids.

(*c*) *The halogen acids* and *sulphuretted hydrogen* unite directly with *ammonia.* The thermal effect of this reaction can be easily calculated in the following manner from the numbers already given: To take an example; an aqueous solution of ammonium chloride can be formed in two ways: *either* 1 gram-molecule of HCl and 1 gram-molecule of NH_3 are first allowed to unite directly, and the resulting compound is subsequently dissolved in water; *or* 1 gram-molecule of HCl and 1 gram-molecule of NH_3 are first separately dissolved in water, and then the neutralization is effected by mixing the solutions formed. But since the initial and final states of the reacting substances are the same in each process, it naturally follows that the sum of the thermal effects in the two cases will also be equal (see page 9). We can express this in the form of an equation—

$$\left.\begin{matrix}(NH_3, HCl)\\ (NH_4Cl, Aq)\end{matrix}\right\} = (NH_3, Aq)+(HCl, Aq)+(NH_3Aq, HClAq).$$

By means of the values already mentioned we obtain—

$Q=$	Cl	Br	I	SH
(NH_3, Aq)	8,435 c	8,435 c	8,435 c	8,435 c
(QH, Aq)	17,314	19,936	19,207	4,560
$(NH_3Aq, QKAq)$	12,270	12,270	12,270	6,196
$-(NH_4Q, Aq)$	3,880	4,380	3,550	3,250
(NH_3, QH)	41,899 c	45,021 c	43,462 c	22,441 c

Thus the thermal effect due to the direct *union of the gaseous hydrides of chlorine, bromine, and iodine with gaseous ammonia* to form solid substances is very large and does not vary much, the mean value being 43,460 c per gram-molecule; in the case of hydrogen sulphide the formation of $NH_4.SH$ produces only about half the amount of heat.

If to these numbers we add the thermal effect due to the formation of 1 gram-molecule of NH_3 and of respectively 1 gram-molecule of HCl, HBr, HI, or H_2S, we obtain the heats of formation of the corresponding four compounds from their respective elements. The values are as follows:—

$(NH_3, HCl) = 41,899$ c	$(N, H_4, Cl) = 75,787$ c
$(NH_3, HBr) = 45,021$	$(N, H_4, Br) = 65,348$
$(NH_3, HI) = 43,463$	$(N, H_4, I) = 49,313$
$(NH_3, H_2S) = 22,441$	$(N, H_5, S) = 37,058$

Thus the formation from their elements of the three analogous salts, the chloride, bromide, and iodide of ammonium, produces very unequal thermal values.

4. Hydrocarbons.

The heats of formation of the hydrocarbons are derived from their heats of combustion; and since the products are carbon dioxide and water, the values are calculated by means of the following equation:—

$$f.\, C_a H_{2b} = a\,(CO_2) + b\,(H_2, O) - (C_a, H_{2b}),$$

where the function f expresses the heat of combustion of the substance. The heat of formation is consequently the difference between the heats of combustion of the elements and that of the compound formed.

Carbon, as is well known, forms a very large number of hydrogen compounds, of which the majority belong to the group of organic substances, and these will be described in detail in a subsequent chapter. Here I shall mention only the experimental results with respect to the first member of some

of the most characteristic groups of homologous hydrocarbons, namely, methane and ethane, ethylene, acetylene, and benzene.

The *heats of combustion* of these five hydrocarbons are as follows :—

Methane . .	CH_4	211,930 c
Ethane . . .	C_2H_6	370,440
Ethylene . .	C_2H_4	333,350
Acetylene . .	C_2H_2	310,059
Benzene . .	C_6H_6	799,350, for vapour at 18°

If now we put the heat of combustion of hydrogen as equal to 68,360 c and that of carbon equal to 96,960 c, we obtain the *heat of formation* at constant pressure of

$(C, H_4) =$ 21,750 c
$(C_2, H_6) =$ 28,560
$(C_2, H_4) = -$ 2,710
$(C_2, H_2) = -47,770$
$(C_6, H_6) = -12,510$, for vapour at 18°

Judging from these figures it would appear that carbon has only a very small affinity for hydrogen, and this agrees with the experience that a direct combination can only take place when carbon and hydrogen are acted upon by the energy of the electric arc;[1] by this process acetylene is formed, the heat of formation of which is strongly negative. We cannot, however, draw any conclusion from these numbers with reference to the affinity relations of carbon and hydrogen, for carbon is a solid body, whilst the hydrocarbons are gases, so that a part of the energy must be used up in transforming the carbon from the amorphous to the gaseous state, and, as a result of this consumption of energy, the calculated heat of formation falls appreciably lower than it would do if the carbon had been in a gaseous condition before the reaction took place. That the consumption of energy due to the conversion

[1] Note by translator: Recent experiments by Bone (*Trans. Chem. Soc.*, 1897, 41 and 1901, 1042) have shown that union takes place at a red heat, and that equilibrium is established between CH_4, C_2H_2, and H_2.

of carbon from the amorphous to the gaseous state is very considerable, namely, 38,380 c for 1 gram-atom of amorphous carbon, will be shown in the chapter on organic substances.

B.—Oxygen Compounds of the Non-metals.

1. Oxides and Acids of Chlorine, Bromine, and Iodine.

(*a*) *Hypochlorous acid.*—The heat of formation of hypochlorous acid in aqueous solution has been determined in two ways: partly by the action of chlorine upon an aqueous solution of potassium hydroxide, by which means a hypochlorite is *formed*, and partly by acting upon hydrogen iodide with hypochlorous acid in aqueous solution, when the acid is *decomposed* with the formation of iodine, water, and hydrogen chloride. Both methods give concordant results, namely, 29,973 c and 29,895 c for the formation of 1 gram-molecule of hypochlorous acid in aqueous solution; thus—

$$(H, Cl, O, Aq) = 29{,}934 \text{ c.}$$

The *heat of absorption* of the anhydride, Cl_2O, was measured directly by passing the gas into water. The gas was prepared by passing dry chlorine through a gas-tube, three metres in length, filled with mercuric oxide, from which the gas was led directly into the calorimeter. The amount of gas absorbed was estimated by titration of the solution formed with stannous chloride and potassium permanganate. The result was—

$$(Cl_2O, Aq) = 9440 \text{ c.}$$

Now, since

$$2(H, Cl, O, Aq) = (Cl_2, O) + (H_2, O) + (Cl_2O, Aq),$$

we obtain the *heat of formation of the anhydride* Cl_2O,

$$(Cl_2, O) = -17{,}929 \text{ c}$$
$$(Cl_2, O, Aq) = -8{,}489 \text{ c.}$$

Thus the heat of formation is *negative*, which is in agreement with the known properties of the substance; for it cannot be formed directly, and is readily decomposed by a

slight rise of temperature, with explosive violence and a great evolution of heat, into chlorine and oxygen. On the other hand, it is easily formed by the action of chlorine upon hydroxides, by acting upon an aqueous solution of the alkalies, or in the reaction with different oxides in the dry state, mercuric oxide being usually preferred. In this case the reaction is

$$(Hg, Cl_2) + (Cl_2, O) - (Hg, O) = R,$$

and as

$$(Hg, Cl_2) - (Hg, O) = 32{,}490 \text{ c}$$

the heat of reaction will be positive, since

$$R = 32{,}490 \text{ c} - 17{,}929 \text{ c} = 14{,}561 \text{ c}.$$

The $HgCl_2$ formed unites at the same time with the undecomposed HgO to give an oxychloride, whereby the heat-evolution is still further augmented. In this method of preparing Cl_2O care must be taken not to have too rapid a stream of chlorine; for otherwise the temperature will rise sufficiently to decompose the Cl_2O formed into chlorine and oxygen.

(*b*) *Chloric acid.*—The heat of formation of chloric acid can also be determined, either in solution or with the dry substances; namely, by the decomposition by heat of potassium chlorate, or by the action of chloric acid upon sulphurous acid in aqueous solution. For potassium chlorate is decomposed with the utmost ease by feeble heating, and with an evolution of heat which is sufficient to make the whole mass glow when potassium chlorate, first melted and then finely pulverized, is mixed with dehydrated ferric oxide, and warmed. The evolution of heat on decomposition of the dry chlorate into potassium chloride and oxygen amounts to 9713 c, or

$$(KCl, O_3) = +9713 \text{ c}.$$

From this the heat of formation (H, Cl, O_3, Aq) is calculated as 23,988 c, whilst the reduction in solution leads to a result of 23,893 c for the same process; we consequently have

$$(H, Cl, O_3, Aq) = 23{,}940 \text{ c},$$

whence we can derive in the same manner—

$$(Cl_2, O_5, Aq) = -20{,}480 \text{ c.}$$

The thermal effect on formation of Cl_2O_5 must therefore be strongly negative, namely more so than $-20{,}480$ c, since this value, which refers to the formation of the substance in aqueous solution, includes also the heat of solution of the anhydride.

(*c*) *The dynamics of chemical processes comprise two principles of considerable importance*, namely, the "*Right of the stronger*," and the "*Maintenance of the status quo*." *The first of these is usually exhibited in a striving after the saturation of the strongest affinities, the second in a resistance to any change of molecular configuration.*

Amongst the manifold examples which serve to illustrate the extent to which these fundamental laws assert themselves throughout the course of chemical processes may be mentioned the *relation between chlorine and potassium hydroxide in aqueous solution under varying external conditions.* The reaction always involves 2 molecules of KOH for each molecule of chlorine. At a *low* temperature, produced by cooling the solution, *hypochlorous acid* is formed; at *higher* temperatures *chloric acid* is produced; and, finally, the addition of a little cobaltic oxide to the solution causes the liberation of oxygen in the free state. These three modes of decomposition can be expressed by the following equations, to which the heat of reaction for 3 gram-molecules of chlorine has been appended:—

$$\begin{matrix} 3KOH \\ 3KOH \end{matrix} + 3ClCl = \begin{matrix} 3KOCl \\ 3HOH \end{matrix} + 3KCl \qquad = 73{,}855 \text{ c}$$

$$\begin{matrix} 3KOH \\ 3KOH \end{matrix} + 3ClCl = 3HOH + 5KCl + KClO_3 = 97{,}945$$

$$\begin{matrix} 3KOH \\ 3KOH \end{matrix} + 3ClCl = 3HOH + 6KCl + O_3 \qquad = 113{,}315$$

Thus in the *first* reaction the form of the molecule, ROH, is preserved; in the *second* reaction only half of the molecules retain the formula ROH, but the remainder of the oxygen, however, takes part in the formation of the molecule $KClO_3$; in the *third* reaction, on the other hand, half of the total

oxygen is liberated in the free state. In these three reactions the thermal effect rises from 73,855 to 97,945 c, and finally reaches 113,315 c, which is in complete accordance with the first principle mentioned above.

Similar relations to these play an exceedingly important part in the action of various oxidizing and reducing agents on organic substances. I shall refer to these in greater detail later on.

(*d*) *Hypobromous and bromic acids.*—The heat of formation of *hypobromous acid* in aqueous solution is derived from observations on the action of bromine vapour or bromine water upon an aqueous solution of potassium hydroxide. The result is as follows:—

$$(H, Br, O, Aq) = 26{,}682 \text{ c}$$
$$(H, Br_{gas}, O, Aq) = 29{,}963$$

The last reaction is in complete agreement with the formation of hypochlorous acid in aqueous solution, for which reaction we found above—

$$(H, Cl, O, Aq) = 29{,}934 \text{ c},$$

from which it follows *that an equal thermal effect is produced on formation of hypochlorous and of hypobromous acids in aqueous solution, provided that both the chlorine and the bromine react in the gaseous state.*

We can also, in the usual manner, deduce the thermal effect of the following processes:—

$$(Br_2, O, Aq) = -14{,}993 \text{ c}$$
$$(Br_{2gas}, O, Aq) = -\ 8{,}431;$$

the last number, in accordance with the statement above, will, of course, be equal to the corresponding value for chlorine, namely −8489 c.

The heat of formation of *bromic acid* is derived from the thermal effect of the reduction of bromic acid by means of stannous chloride in aqueous solution, and is equal to

$$(H, Br, O_3, Aq) = \quad 12{,}416 \text{ c}$$
$$(Br_2, O_5, Aq) = -43{,}525.$$

The thermal value for each gram-atom of bromine is 115,24 c lower than for a gram-atom of chlorine in the corresponding reaction, which is approximately the same difference that was found between the heats of formation of hydrochloric and hydrobromic acids in aqueous solution, namely 10,935 c.

(*e*) *Iodic and periodic acids.*—The heat of formation of *iodic acid* is determined in two ways, namely, by the *reduction* of iodic acid by means of hydriodic acid in aqueous solution according to the equation—

$$HIO_3 + 5HI = 3I_2 + 3H_2O;$$

as well as by the *oxidation* of hydriodic acid with hypochlorous acid in aqueous solution according to the equation—

$$HI + 3HClO = HIO_3 + 3HCl.$$

Both these reactions are accompanied by a great evolution of heat, 83,332 c and 70,682 c respectively; and, calculating from these numbers, we obtain 55,884 c and 55,710 c as the *heat of formation of iodic acid in aqueous solution*, or, as a mean value—

$$(H, I, O_3, Aq) = 55{,}797 \text{ c.}$$

From the *heats of solution* of the acid and of the anhydride,

$$(HIO_3, Aq) = -2166 \text{ c}$$
$$(I_2O_5, Aq) = -1792,$$

and from the heat of formation of iodic acid in aqueous solution we obtain the values—

$$(I_2, O_5) = 45{,}029 \text{ c}$$
$$(I_2O_5, H_2O) = 2{,}540$$
$$(H, I, O_3) = 57{,}963$$

which are the *heats of formation of iodic anhydride and of crystalline iodic acid, as well as the heat of hydration of iodic anhydride.*

(*f*) *The heat of formation of periodic acid* is calculated from the thermal effect of its reduction to hydriodic acid in aqueous

solution by means of stannous chloride, with the following result :—

$$(H_5, I, O_6, Aq) = 184{,}400 \text{ c}$$
$$(H, I, O_4, Aq) = 47{,}680$$
$$(I_2, O_7, Aq) = 27{,}000$$

The heat of solution of *crystalline periodic acid* was found to be -1380 c, so that the heat of formation will be

$$(H_5, I, O_6) = 185{,}780 \text{ c}$$
$$(H_5IO_6, Aq) = - 1{,}380$$

(*g*) *The densities or molecular volumes of aqueous solutions of periodic and iodic acids* have been determined over a dilution of from 10 to 320 gram-molecules of water for 1 gram-molecule of acid. For periodic acid at 17° the result was as follows :—

$$H_5IO_6 + nH_2O.$$

n	Density of the solution.	Molecular weight.	Molecular volume.	Volume of the water.	Difference.
20	1·4008	588	419·77	360	59·77
40	1·2165	948	779·30	720	59·30
80	1·1121	1668	1499·9	1440	59·9
160	1·0570	3108	2940·2	2880	60·2
320	1·0288	5988	5820·2	5760	60·0

The last column shows that there is a constant difference, namely 59·8 c.c., between the molecular volume of the solution and the volume of the water of which it is composed, so that the volume of the solution can be expressed by the equation—

$$R_n = 18n + 59{\cdot}8,$$

and the density of the solution will be

$$s_n = \frac{18n + 228}{18n + 59{\cdot}8},$$

an equation which gives an accurate value of the density up to the fourth decimal place; for 228 is the gram-molecular weight of H_5IO_6, whilst 59·8 c.c. is the volume occupied by 1

gram-molecule in aqueous solution. *Thus on dilution of a solution of periodic acid no contraction is found to take place.*

Iodic acid shows somewhat different properties, as will be seen from the following table:—

$HIO_3 + nH_2O$.

n	Density of the solution.	Molecular weight.	Molecular volume.	Volume of the water.	Difference.
10	1·6609	356	214·34	180	34·34
20	1·3660	536	392·37	360	32·37
40	1·1945	896	750·09	720	30·09
80	1·1004	1616	1468·5	1440	28·5
160	1·0512	3056	2907·2	2880	27·2
320	1·0258	5936	5786·8	5760	26·8

The difference between the molecular volume of the solution and the volume of the water contained in it is therefore not a constant for iodic acid, since there is a decrease of the former with increasing amounts of water; from this it is evident that dilution with water causes a contraction, as was also found to be the case with nearly all the substances investigated (see p. 139 *et seq.*). The molecular volume can be calculated from the equation—

$$R_n = 18 . n + 39{\cdot}1 - \frac{n}{n + 18} 13{\cdot}1.$$

For $n = 0$, R_a will be equal to 39·1 c.c., which therefore corresponds to the maximum volume that 1 gram-molecule of iodic acid can occupy in aqueous solution. On dilution of the solution a contraction occurs, in consequence of which the difference in volume gradually decreases until it reaches 26 cc.

(*h*) *Iodine has a positive affinity for oxygen, and in this differs completely from bromine and chlorine.* With reference to the affinity for the three halogens of all the other elements which have been investigated, as, for instance, hydrogen, the metals, carbon, etc., we find that it is greatest for chlorine, less for bromine, and least of all for iodine; *oxygen alone forms an*

exception; for whilst the affinity of oxygen for chlorine is negative, and for bromine still more negative, *the affinity between oxygen and iodine is strongly positive.*

The numerical results of the above-mentioned reactions are as follows :—

$$(Cl_2, O_5, Aq) = -20{,}480 \text{ c}$$
$$(Br_2, O_5, Aq) = -43{,}520$$
$$(I_2, O_5, Aq) = +43{,}240,$$

that is to say, when 2 gram-molecules of the three acids are formed in aqueous solution by the union of chlorine, bromine, or iodine, with oxygen, the thermal effect is negative for chlorine, still more negative for bromine, but strongly positive for iodine. This difference in property is evident from the following comparison :—

R.	(H, R, O_3, Aq).	(H, R, Aq).	$(HRAq, O_3)$.
Cl	23,940 c	39,320 c	−15,380 c
Br	12,420	28,380	−15,960
I	55,800	13,170	+42,630

The figures in column 4 represent the difference between those in columns 2 and 3, and they consequently show that the formation of the acids by the oxidation of the corresponding hydrides in aqueous solution produces *an absorption* of approximately 15,670 c in the case of chlorine and bromine, whilst the oxidation of hydriodic to iodic acid is accompanied by an *evolution* of 42,630 c. Thus the heats of oxidation of hydrochloric and hydrobromic acids are approximately equal to one another and are negative, but the heat of oxidation of hydriodic to iodic acid is some 58,300 c greater than was the case with the two other halides.

The potassium salts of these three acids are known to be decomposed on heating to form oxygen and the chloride, bromide, or iodide of potassium respectively. The thermal effects are—

R	$(K, R)-(K, R, O_3)=-(KR, O_3)$.
Cl	105,610 c − 95,840 c = + 9,970 c
Br	95,310 − 84,062 = +11,248
I	80,130 − 124,489 = −44,359

Thus potassium chlorate and potassium bromate are decomposed to oxygen and the respective chloride and bromide with a large evolution of heat (see preceding table), whilst the decomposition of potassium iodate is accompanied by a considerable absorption of heat.

These results all tend to show that the *affinity of iodine for oxygen is strongly positive*, which was already apparent from the well-known fact that iodic acid can be formed by the oxidation of iodine with strong nitric acid, as well as by the ease with which potassium iodate is formed on heating potassium chlorate with iodine.

(*i*) *Constitution of iodic acid.*—Whilst the iodine in hydriodic acid and in most other compounds behaves precisely similarly to chlorine and bromine in the corresponding cases, yet nevertheless the constitution of iodic acid must, from the above-mentioned facts, be of an entirely different character from that of bromic and chloric acids. The facility with which iodic acid is converted into the anhydride suggests that it is not of a monobasic character; furthermore, iodic acid forms acid salts, whilst this is not the case with chloric and bromic acids; and when we remember that the majority of the iodates, with the exception of those of the alkali metals, are sparingly soluble, whilst the monobasic acids, such as bromic, chloric, nitric, phosphorous, acetic, etc., form almost exclusively soluble salts, it seems in the highest degree probable that *iodic acid is dibasic* with the molecular formula $H_2I_2O_6$.

Also, if we regard the double molecule of iodic acid as dibasic, there will then be a great similarity to periodic acid, proved by my researches (see p. 103) to be dibasic, and which also forms characteristic acid salts.

2. Oxides and Acids of Sulphur.

(*a*) *Sulphur dioxide.*—A knowledge of the *heat of combustion of rhombic sulphur* is essential to the determination of the heat phenomena on formation of the oxides and acids of sulphur. To prepare it, sulphur is crystallized from a solution of carbon disulphide, separated from any adherent solution at the filter pump, and finally exposed to a current of air at 95° for about six hours in order to remove the last traces of carbon disulphide. The resulting product consists of small, transparent rhombic crystals. The combustion was carried out in pure dry oxygen, and the weight of the sulphur burned as well as that of the product formed was determined; as is well known, a little sulphur trioxide is always formed at the same time as the dioxide. Calculating from the weight of sulphur used, which in three experiments amounted to 8·009 grams, we find a heat of combustion of 71,080 c; calculating from the products, one of 71,113 c. I regard the first number as the more accurate, since a determination of the products of combustion is always attended by some uncertainty, and prefer the value—

$$(S, O_2) = 71{,}080 \text{ c for rhombic sulphur.}$$

I have also determined the heat of combustion of freshly prepared monoclinic sulphur, and found

$$(S, O_2) = 71{,}720 \text{ c for monoclinic sulphur.}$$

Monoclinic sulphur, therefore, has a greater heat of combustion than rhombic, and this agrees with the fact that the monoclinic variety is converted into the rhombic with evolution of heat.

The heat of absorption of gaseous SO_2, and similarly also the *heat of solution of liquid* SO_2, was measured at the same temperature, approximately 19° C. In the former experiments 19·459 grams of gaseous SO_2 were absorbed, 250 gram-molecules of water being used for each gram-molecule of SO_2; in the latter, 22·42 grams of liquid SO_2 were dissolved in an amount of water equal to 300 gram-molecules for each gram-molecule of SO_2. The last-mentioned experiments were carried

out in the following manner. A tube of known capacity, containing the liquified SO_2, was drawn out to a fine point and placed in the water of the calorimeter with the point downwards. When the temperature had adjusted itself, and the thermometer had been read, the point of the tube was broken off by gentle pressure on the bottom of the calorimeter, and the liquid SO_2 flowed out into the water and was absorbed. The following were the experimental results :—

$(SO_2, Aq) = 7700$ c for the absorption of gaseous SO_2
$[SO_2, Aq] = 1500$ c for the solution of liquid SO_2.

The difference between these two numbers amounts to 6200 c, and corresponds to the heat of vaporization of 1 gram-molecule of liquid SO_2 at 19° ; whence it follows that the thermal effect on formation of the *liquid* dioxide from its elements is

$[S, O_2] = 77{,}280$ c for rhombic sulphur.

(*b*) *Sulphuric acid and sulphur trioxide.*—Aqueous sulphurous acid was oxidized with pure, dry chlorine in a platinum flask, of about $1\frac{1}{2}$ litre capacity, which was placed in the calorimeter. Owing to the very large amount of heat evolved it is not advisable that the sulphurous acid solution should contain more than two parts of the anhydride in a thousand. The progress of the reaction is determined by precipitating the hydrochloric acid formed with silver nitrate and weighing the silver chloride formed. The result of the experiments was—

$$(SO_2Aq : Cl_2) = (SO_2Aq, O) + 2(H, Cl, Aq) - (H_2, O) = 73{,}907 \text{ c.}$$

From this number, and the known values for the heat of solution of sulphur dioxide, and also of the heats of formation of hydrochloric acid and water, it follows that

$$(SO_2Aq, O) = 63{,}634 \text{ c}$$
$$(SO_2, O, Aq) = 71{,}334,$$

and since (S, O_2) is equal to 71,080 c, we obtain

$$(S, O_3, Aq) = 142{,}414 \text{ c}$$

as the thermal effect on formation of an aqueous solution of sulphuric acid from its elements. If, finally, we subtract from

this value the heat of solution of liquid sulphuric anhydride (see p. 47),

$$(SO_3, Aq) = 39{,}170 \text{ c for the liquid anhydride,}$$

we arrive at the *heat of formation of sulphuric anhydride itself*,

$$(S, O_3) = 103{,}240 \text{ c for the liquid anhydride,}$$

whilst for the formation of liquid sulphur dioxide we found above,

$$[S, O_2] = 77{,}280 \text{ c for the liquid anhydride.}$$

The compounds considered above were both in the liquid condition; but sulphur itself is a solid body, it is therefore advisable, for purpose of comparison, to calculate the thermal effect starting from molten sulphur, and at *constant volume*. This is done by adding on the heat of fusion of sulphur, which according to *Person* is 300 c, and by subtracting an amount of heat equal to 580 c for each gram-molecule of gas which enters into the compound; we then have :—

	Trioxide.	Dioxide.
Heat of formation	103,240 c	77,280 c
„ fusion of 32 grams of sulphur .	+300	+300
Reduction to constant volume . . .	−870	−580
Sum . .	102,670 c	77,000 c
or . . .	4 × 25,668 c	3 × 25,667 c

Thus we see that the *heats of formation of the trioxide and dioxide are in the exact ratio of* 4 : 3. Similar simple relations are frequently found to exist between the heats of formation of the different oxides of one and the same substance.

The heat of formation of *sulphuric acid*, H_2SO_4, is found from the numbers already given to be

$$(H_2, S, O_4) = (S, O_3) + (H_2, O) + (SO_3, H_2O)$$
$$192{,}920 \text{ c} = 103{,}240 \text{ c} + 68{,}360 \text{ c} + 21{,}320 \text{ c.}$$

(*c*) *Sulphurous acid.*—The heat of formation was determined by oxidation of the sodium salt with hypochlorous acid in aqueous solution, whereby sodium sulphate, sodium chloride, sulphuric acid, and hydrochloric acid were formed. The

reaction is rapid, and gives satisfactory results. From the thermal effect of the process

$$(Na_2S_2O_3Aq : 4HClO) = 251{,}624 \text{ c},$$

we can calculate the heat of formation

$$(S_2, O_2, Aq = 69{,}470 \text{ c}$$
$$(H_2, S_2, O_3, Aq) = 137{,}830$$

The heat of formation of *dithionic acid* is deduced from the thermal effect due to the decomposition by heat of the potassium salt into potassium sulphate and sulphur dioxide. This experiment shows that the decomposition is not attended by any measurable thermal change, and that consequently

$$(K_2, S, O_4) + (S, O_2) = (K_2, S_2, O_6).$$

From this we calculate that

$$(S_2, O_5, Aq) = 211{,}080 \text{ c}$$
$$(H_2, S_2, O_6, Aq) = 279{,}440$$

The heat of formation of *tetrathionic acid* is derived from the thermal effect on oxidation of sodium thiosulphate with iodine in aqueous solution, when sodium tetrathionate and sodium iodide are formed. The value is—

$$(2Na_2S_2O_3Aq : I_2) = 7954 \text{ c},$$

from which we calculate that

$$(S_4, O_5, Aq) = 192{,}430 \text{ c}$$
$$(H_2, S_4, O_6, Aq) = 206{,}790$$

(*d*) *The sulphur acids* have therefore the following heats of formation :—

$(S, O_2, Aq) = 78{,}780$ c	$(H_2, S, O_3, Aq) = 147{,}140$ c
$(S_2, O_2, Aq) = 69{,}470$	$(H_2, S_2, O_3, Aq) = 137{,}830$
$(S_2, O_5, Aq) = 211{,}080$	$(H_2, S_2, O_6, Aq) = 279{,}440$
$(S_4, O_5, Aq) = 192{,}430$	$(H_2, S_4, O_6, Aq) = 260{,}790$
$(S, O_3, Aq) = 142{,}410$	$(H_2, S, O_4, Aq) = 210{,}770$

These values demonstrate that the *affinity of sulphur for oxygen is very great.* It is also interesting to note that there is a difference of 9310 c between the heats of formation of sulphurous and of thiosulphuric acids in aqueous solution,

whilst the difference in the case of dithionic and tetrathionic acids is 18,650 c, that is, double as great; in the first instance 1 gram-atom of sulphur is taken up, in the second 2 gram-atoms, so that consequently the *addition of sulphur is attended by a heat absorption of some* 9320 *c for every gram-atom.*

It should also be remarked that the formation of dithionic from sulphurous acid, and of tetrathionic from thiosulphuric acid, are entirely analogous processes, namely—

$$2SO_2Aq + O = S_2O_5Aq \qquad 2S_2O_2Aq + O = S_4O_5Aq$$

and this process of oxidation corresponds to

$$(2SO_2Aq,\ O) = 53{,}520 \text{ c}$$
$$(2S_2O_2Aq,\ O) = 53{,}490$$

The thermal effect is therefore precisely the same, *which proves that the two processes are of a uniform character.*

Trithionic and pentathionic acids.—Since it has been shown above that the taking up of 1 gram-atom of sulphur involves a diminution of 9320 c in the thermal effect, we can, without direct experiment, predict the probable heats of formation of these two acids; for they must be 9320 c less than those of dithionic and tetrathionic acids respectively. We shall, by this means, have the following heats of formation for the four thionic acids in aqueous solution:—

Dithionic acid	$(S_2,\ O_5,\ Aq) = 211{,}080$ c
Trithionic acid	$(S_3,\ O_5,\ Aq) = 201{,}760$
Tetrathionic acid . . .	$(S_4,\ O_5,\ Aq) = 192{,}430$
Pentathionic acid . . .	$(S_5,\ O_5,\ Aq) = 183{,}110$

For further comparative details see Table 18.

3. Oxygen Compounds of Selenium and Tellurium.

(*a*) *Selenious acid.*—A solution of selenium dioxide in hydrochloric acid is reduced by sodium hydrosulphide in the following manner:—

$$SeO_2 + 2HCl + 2NaSH = 2NaCl + 2H_2O + Se + S_2$$

The thermal effect of this process was measured, and amounted to 73,398 c; from which we calculate that

$$(Se, O_2, Aq) = 56{,}336 \text{ c.}$$

Some twelve years later I controlled the accuracy of this value by the direct measurement of the heat of formation of $SeCl_4$ (46,156 c) and of the thermal effect on decomposition of the chloride with water (30,370 c). In this decomposition hydrochloric and selenious acids are formed, and their heats of formation can therefore be derived from the numbers given by means of the equation—

$$(SeCl_4 : Aq) = 4(H, Cl, Aq) - 2(H_2, O) - (Se, Cl_4) + (Se, O_2Aq)$$
$$30{,}370 \text{ c} = 157{,}260\text{c} - 136{,}720\text{c} - 46{,}156 + (Se, O_2, Aq)$$

from which it is found that

$$(Se, O_2, Aq) = 55{,}986 \text{ c.}$$

The difference between this value and the one found above amounts only to 350 c; the agreement is therefore very satisfactory, when we remember that the two numbers were obtained by entirely different methods. I have adopted the mean value—

$$(Se, O_2, Aq) = 56{,}161 \text{ c}$$

as the heat of formation of selenious acid in aqueous solution.

For the *heat of solution of selenium dioxide* I found

$$(SeO_2, Aq) = -918 \text{ c,}$$

whence it follows that the *heat of formation* is

$(Se, O_2) = 57{,}079$ c. for the crystalline anhydride.

The negative heat of solution is in accordance with the fact that selenium dioxide, similarly to sulphur dioxide, does not form a hydrate when dissolved in water.

(*b*) *Selenic acid.*—In aqueous solution selenious and hypochlorous acids react to form selenic and hydrochloric acids. The thermal effect produced is 29,882 c, whence it follows that

$$(SeO_2Aq, O) = 20{,}501 \text{ c}$$
$$(Se, O_3, Aq) = 76{,}662$$
$$(H_2, Se, O_4, Aq) = 145{,}020$$

Now, since the *heat of solution* of liquid H_2SeO_4 was determined by Metzner (*Compt. rendus*, cxxiii. 998, Dec., 1896) as 16,800 c, it follows that

$$(H_2, Se, O_4) = 128{,}220 \text{ c for the liquid acid.}$$

Comparing this number with the one found above for the corresponding reaction, namely, the formation of liquid H_2SO_4 from its elements, we arrive at the remarkable result that

$$\left.\begin{aligned}(H_2, S, O_4) &= 192{,}920 \text{ c} = 3 \cdot 64{,}307 \text{ c} \\ (H_2, Se, O_4) &= 128{,}220 \quad = 2 \cdot 64{,}110\end{aligned}\right\} \text{ for the liquid acids.}$$

The heats of formation of sulphuric and selenic acids are thus in the exact ratio of 3 : 2, when the two acids are compared in the liquid condition.

(*c*) *Tellurous acid.*—The heat of formation, similarly to that of selenious acid, is derived from the following measurements:—

$$(Te, Cl_4) = 77{,}377 \text{ c}$$
$$(TeCl_4 : Aq) = 20{,}345,$$

that is, from the thermal effect due to the formation of the tetrachloride and of its subsequent decomposition by water; the number 20,345 c applies to the complete decomposition. The calculated value is

$$(Te, O_2, H_2O) = 77{,}176 \text{ c}$$

for the heat of formation of 1 gram-molecule of solid tellurous acid.

(*d*) *Telluric acid.*—Tellurous acid dissolves in dilute nitric or hydrochloric acids without appreciable thermal effect; the process can therefore also be expressed as

$$(Te, O_2, Aq) = 77{,}176 \text{ c.}$$

On oxidation of the dissolved acid to the telluric state by means of potassium permanganate, an evolution of 39,837 c is produced; and if we subtract therefrom the thermal effect due to the decomposition of the oxidizing agent (*i.e.* 18,632 c) we obtain—

$$(TeO_2Aq, O) = 21{,}205 \text{ c}$$
$$(Te, O_3, Aq) = 98{,}380$$
$$(H_2, Te, O_4, Aq) = 166{,}740$$

In the following table will be found a comparison of the three principal values representing the *affinity of oxygen for sulphur, selenium, and tellurium* :—

	Sulphur.	Selenium.	Tellurium.
(R, O_2, Aq)	78,780 c	56,160 c	77,180 c
(R, O_3, Aq)	142,410	76,660	98,380
(RO_2Aq, O)	63,630	20,500	21,200

The first line shows that the *affinity of selenium for oxygen is less than that of sulphur*, and we should therefore expect that that of tellurium would be even smaller ; but, on the contrary, *tellurium has a far greater affinity for oxygen than has selenium.* This behaviour calls to mind the relation of oxyen to the halogens, for the affinity of bromine for oxygen is less than that of chlorine, whilst that of iodine is far greater. Similar relations are found in the *P, As, Sb* group, and from this it would appear that the *first two members of each group, as, for example, Cl and Br, S and Se, P and As, resemble each other more closely than they do the third member of the series.*

The greatest difference between sulphur on the one hand, and selenium and tellurium on the other, is observed in the passage from the lower to the higher state of oxidation ; for whilst the thermal effect due to the oxidation of sulphurous to sulphuric acid amounts to 63,630 c, a similar oxidation of selenious and tellurous acid produces only one-third of this value.

4. Oxides and Acids of Nitrogen.

(*a*) The determination of the heats of formation of the oxides and acids of nitrogen is based upon the following calorimetric researches :—

a. Decomposition of ammonium nitrite by heating a concentrated solution ; which decomposition is attended

by an evolution of 71,770 c, calculated for the anhydrous salt, thus

$$-(N_2, 2H_2O) = 71{,}770 \text{ c},$$

from which it follows that

$$(N_2, H_4, O_2) = 2(H_2, O) + (N_2, 2H_2O) = 136{,}720 \text{ c} - 71{,}770 \text{ c}$$
$$(N_2, H_4, O_2) = 64{,}950 \text{ c}.$$

β. Direct oxidation of 2 gram-molecules of NO by 1 gram-molecule of O_2 to form 1 gram-molecule of N_2O_4; the thermal effect calculated for the molecule N_2O_4 in the *non-dissociated* state is

$$(2NO, O_2) = 40{,}500 \text{ c}.$$

γ. Thermal effect on solution of 1 gram-molecule of *non-dissociated* N_2O_4 in water, for which reaction it was found that

$$(N_2O_4, Aq) = 14{,}150 \text{ c}.$$

δ. Oxidation of an aqueous solution of N_2O_4 by means of chlorine or potassium permanganate, which gives us the thermal effect of the reaction (N_2O_4Aq, O), the values obtained being 18,277 c and 18,367 c respectively, or, as a mean value—

$$(N_2O_4Aq, O) = 18{,}320 \text{ c}.$$

ϵ. Thermal effect on combustion of hydrogen or carbon monoxide in *nitrous oxide*, from which the heat of formation of this oxide was calculated as $-18{,}010$ c and $-17{,}470$ c respectively; as a mean value—

$$(N_2, O) = 17{,}740 \text{ c}.$$

The heats of formation of the remaining oxygen compounds can then be deduced from the first four of the reactions described above in the following manner:—

(*b*) *Nitric acid.*—By adding together the values found in reactions β, γ, and δ, we obtain the heat of formation of nitric acid from nitric oxide, oxygen, and water in aqueous solution; thus

$$(2NO, O_2) + (N_2O_4, Aq) + (N_2O_4Aq, O) = (2NO, O_3, Aq),$$

from which it follows that

$$(2NO, O_3, Aq) = 72{,}970 \text{ c};$$

moreover, since

$$(2NO, O_3, Aq) + (H_2, O) = 2(H, NO, O_2, Aq)$$

we obtain

$$(H, NO, O_2, Aq) = 70{,}665 \text{ c.}$$

(*c*) *Nitrous acid.*—When the molecule N_2O_4 is dissolved in water we can assume the decomposition to take place in two ways, namely, either according to the equation—

$$2N_2O_4 + Aq = N_2O_5Aq + N_2O_3Aq \quad . \quad . \quad (1)$$

whereby nitric and nitrous acids are formed, or according to the equation—

$$3N_2O_4 + Aq = 2NO + 2N_2O_5Aq \quad . \quad . \quad (2)$$

That the last-named process, however, does not occur in dilute solution can be shown from the values obtained in β, γ, and δ. For, in this case, since 1 molecule of N_2O_4 loses 1 molecule of O_2 in oxidizing the remaining 2 molecules of N_2O_4 to N_2O_5, the thermal effect would be expressed by the equation—

$$3(N_2O_4, Aq) = -(2NO, O_2) + 2(N_2O_4, O, Aq) \quad (3)$$

But

$$(N_2O_4, O, Aq) = (N_2O_4, Aq) + (N_2O_4Aq, O),$$

and substituting this value in equation (3) we obtain

$$(2NO, O_2) + (N_2O_4, Aq) = 2(N_2O_4Aq, O). \quad (4)$$

that is to say, $\beta + \gamma = 2\delta$; but $\beta + \gamma$ is equal to 54,650 c, whilst 2δ is equal to 36,640 c; and since the equation is not satisfied, the assumption upon which it was based must be incorrect. Decomposition must therefore occur according to equation (1); in which 2 *molecules of* N_2O_4 *are decomposed by water with the formation of* N_2O_3Aq *and* N_2O_5Aq. We therefore have—

$$2(2NO, O_2) + 2(N_2O_4, Aq) = (2NO, O, Aq) + (2NO, O_3, Aq),$$

or

$$2\beta + 2\gamma = (2NO, O, Aq) + 72{,}970 \text{ c},$$

whence it follows that

$$(2NO, O, Aq) = 36{,}330 \text{ c}$$

and also

$$(H, NO, O, Aq) = 52{,}345 \text{ c.}$$

(*d*) *Nitric oxide, NO.*—According to α the heat of formation of ammonium nitrite equals 64,950 c; from which it follows that on solution of the salt in water

$$(N_2, H_4, O_2) + (N_2H_4O_2, Aq) = (N, H_3, Aq) + (H, N, O_2, Aq) + (NH_3Aq, HNO_2Aq).$$

If, in the equation above, we insert the following values:—

$$\left.\begin{aligned}(N_2, H_4, O_2) &= \ 64{,}950 \text{ c}\\ (N, H_3, Aq) &= \ 20{,}320\\ (N_2H_4O_2, Aq) &= -\ 4{,}750\\ (NH_3Aq, HNO_2Aq) &= +\ 9{,}110\end{aligned}\right\} \text{Berthelot}$$

we obtain the thermal effect corresponding to the unknown term, namely—

$$(H, N, O_2, Aq) = 30{,}770 \text{ c.}$$

Moreover, since

$$(H, N, O_2, Aq) = (N, O) + (H, NO, O, Aq),$$

and the last term of this equation was found above to equal 52,345 c, we have as the *heat of formation of nitric oxide*—

$$(N, O) = -21{,}575 \text{ c.}$$

(*e*) *The heats of formation of the oxides and acids of nitrogen* can now be deduced from the thermal data already recorded—

Reaction.	Thermal effect.	Remarks.
$(N_2, O) =$	$-17{,}740$ c	
$(N, O) =$	$-21{,}575$	
$(N, O_2) =$	$-\ 8{,}125$	Completely dissociated.
$(N_2, O_4) =$	$-\ 2{,}650$	Non-dissociated.
$(NO_2, NO_2) =$	$13{,}600$	Heat of dissociation of N_2O_4.
$(N_2, O_3, Aq) =$	$-\ 6{,}820$	Formation in aqueous solution.
$(N_2, O_5, Aq) =$	$+29{,}820$	
$(H, N, O_2, Aq) =$	$30{,}770$	
$(H, N, O_3, Aq) =$	$49{,}090$	
$(H, N, O_3) =$	$41{,}600$	Nitric acid.
$(HNO_3, Aq) =$	$7{,}480$	Heat of solution.

Reaction.	Thermal effect.	Remarks.
$(2NO, O, Aq)$ =	36,330	
$(2NO, O_3, Aq)$ =	72,970	
$(2NO, O_2)$ =	40,500	Non-dissociated.
(N_2O_4, Aq) =	14,150	
(N_2O_4Aq, O) =	18,320 = (HNO_2Aq, O)	

This table shows that the affinity of nitrogen for oxygen is, or at least appears to be, negative; even for the highest degree of oxidation, namely N_2O_5, the thermal effect is approximately equal to zero when the oxide is formed directly in the absence of water. The explanation of this general negative character must be sought for in the heat of formation of NO, for the table shows that—

$$N_2 + O_2 = 2NO - 43{,}150 \text{ c}$$
$$2NO + O_2 = 2NO_2 + 26{,}900$$
$$NO + NO = N_2O_4 + 13{,}600$$
$$2NO + O_2 = N_2O_4 + 40{,}500$$

Thus whilst the first gram-molecule of oxygen, which combines with 1 gram-molecule of nitrogen to form 2 gram-molecules of NO, produces a *heat-absorption* of 43,150 c, the union with the second gram-molecule, by means of which 1 gram-molecule of N_2O_4 is formed from 2 gram-molecules of NO, takes place with an evolution of 40,500 c. This is in complete agreement with the fact that NO unites directly with oxygen without the aid of any external agency, which is a case of true combustion without ignition.

The third equation gives the *heat of dissociation of* N_2O_4; for at constant pressure this compound splits up to form 2 gram-molecules of NO_2 with an absorption of 13,600 c.

If we take NO as the starting-point in expressing the heat of formation of nitrous and nitric acids in aqueous solution, we see from the table that

$$(2NO, O, Aq) = 36{,}330 \text{ c}$$
$$(2NO, O_3, Aq) = 72{,}970 \quad = 2 \times 36{,}485 \text{ c.}$$

Here, again, we have an example of the simple ratio which exists between the heats of formation for different degrees of oxidation.

The large amount of heat which is absorbed in the formation of NO and N_2O must certainly, from what has been said above, arise from there being a considerable consumption of energy in the breaking up of the nitrogen and oxygen molecules on direct formation of the oxides of nitrogen. This point will be discussed more fully in a subsequent chapter.

5. Acids of Phosphorus.

(*a*) *General properties of the acids.*—The three acids, hypophosphorous, phosphorous, and orthophosphoric, can all be obtained in a crystalline form by evaporating an aqueous solution of the pure acids until the boiling-point of the liquid, namely, 130°, 180°, and 215° respectively, is reached. On cooling, phosphorous acid crystallizes out at once, phosphoric acid not, as a rule, until a crystal has been introduced into the melted acid, whilst crystallization of the fused hypophosphorous acid is only brought about at a very low temperature and when the walls of the vessel are rubbed with a glass rod.

Since the acids can all be obtained as liquids at about 18°, the densities and molecular volumes of the *liquid acids* can be easily determined, as well as the *melting-points of the crystalline acids.* The values found are contained in the following table:—

Acid.	Melting-point.	Liquid acid.		
		Density at 18°.	Molecular weight.	Molecular volume.
H_3PO_4	38·6°	1·884	98 gr.	52·02 cc
H_3PO_3	70·1	1·651	82	49·66
H_3PO_2	17·4	1·493	66	44·20

Thus the densities of the liquid acids rise appreciably from hypophosphorous to phosphoric acid; but, since the molecular weights increase at the same time, there is only a moderately small difference in the molecular volumes of the three acids.

The heat of fusion of the acids, that is to say, the amount of heat which becomes latent on passing from the crystalline to the liquid acid, can be easily determined; for it is equal to the difference between the *thermal values* obtained when the *crystallized and liquid acids are dissolved in water* under the same external conditions (temperature and amount of water). The following table contains the heats of solution as well as the heats of fusion :—

Acid.	Heat of solution.		Heat of fusion at 18°.
	Cryst. acid.	Liquid acid.	
H_3PO_4	+2690 c	+5210 c	−2520 c
H_3PO_3	− 130	+2940	−3070
H_3PO_2	− 170	+2140	−2310

Thus all the liquid acids dissolve in water with evolution of heat; but, of the crystalline acids, phosphoric alone has a positive heat of solution; in the case of the other two acids the effect is feebly negative. The heats of fusion are equal to the differences between the numbers in the second and third columns.

(*b*) *The heats of formation of the acids* were determined in the following manner. An aqueous solution of *hypophosphorous acid* was oxidized with bromine, when the observed thermal effect gave the value of the direct oxidation of hypophosphorous to phosphoric acid in aqueous solution. The result was—

$$(H_3PO_2Aq,\ O_2 = 165{,}490 \text{ c.}$$

A similar oxidation of an aqueous solution of *phosphorous* to phosphoric acid by means of bromine gave the following heat of oxidation :—

$$(H_3PO_3Aq,\ O) = 77{,}720 \text{ c.}$$

There still remains to be determined the thermal effect on formation of *orthophosphoric acid* itself from phosphorus and oxygen; and for this purpose I made use of the reduction of

a very dilute aqueous solution of iodic acid by means of free phosphorus. The iodic acid solution had the composition $HIO_3 + 2400H_2O$; a stronger solution was unnecessary, since the temperature on reduction of the solution in question rose about 4·7°. In this experiment a very dilute solution of iodic acid was treated with an excess of phosphorus, so that the iodic acid was completely reduced to hydriodic acid. After the thermal effect had been measured, the *liquid was quantitatively analyzed* in the following manner: 500 grams of the liquid were completely oxidized to phosphoric acid by means of bromine, free bromine and iodine were converted into halogen acids by means of sodium thiosulphate, and finally the amount of phosphoric acid was determined as magnesium pyrophosphate. In this manner it was found in the five experiments that for every molecule of iodic acid from 1·600 to 1·630 atoms of phosphorus went into solution, partly as phosphorous, partly as phosphoric acid. Now, since the difference between the heats of formation of these two acids is known from the preceding researches, the last experiments give the thermal effect on formation of a gram-molecule of both of the acids from their elements, namely:—

$$(H_3, P, O_4, Aq) = 305{,}290 \text{ c}$$
$$(H_3, P, O_3, Aq) = 227{,}570$$

It is noteworthy that the proportion in which the two acids are formed on oxidation of phosphorus is almost constant. If phosphorous acid only is formed, for every molecule of HIO_3 two atoms of phosphorus must be acted upon; for the exclusive formation of phosphoric acid, on the other hand, 1·2 atoms of phosphorus are taken up. Now, the value found for the number of atoms of phosphorus acted upon lies between 1·600 and 1·630, whilst the mean of 2 and 1·2 is 1·600. We can therefore assume, at least approximately, that on *oxidation of phosphorus by a dilute solution of iodic acid, one half of the iodic acid leads to the production of phosphorous acid, the other half to phosphoric acid.*

Now, since the heats both of solution and of fusion of the three acids have been determined, the thermal effect of their

formation from their elements can also be calculated. The results are compared in the following table:—

State of the acid formed.	Reaction.	Thermal effect.	Difference.
Crystalline acids	(H_3, P, O_4)	302,600 c	74,900 c
	(H_3, P, O_3)	227,700	87,730
	(H_3, P, O_2)	139,970	
Liquid acids	(H_3, P, O_4)	300,080	75,450
	(H_3, P, O_3)	224,630	86,970
	(H_3, P, O_2)	137,660	
Aqueous solutions	(H_3, P, O_4, Aq)	305,290	77,720
	(H_3, P, O_3, Aq)	227,570	87,770
	(H_3, P, O_2, Aq)	139,800	
Aqueous solutions	(P_2, O_5, Aq)	405,500	155,440
	(P_2, O_3, Aq)	250,060	175,540
	(P_2, O, Aq)	74,520	

The affinity of phosphorus for oxygen is in all cases very great, but it is nevertheless smaller than that of some of the metals, as, for instance, Mg, Ca, etc. I may add that I attempted to estimate the heat of solution of phosphoric anhydride by direct solution in water. The reaction, as is well known, is very violent, so that the result is always attended by some uncertainty; the value found was—

$$(P_2O_5, Aq) = 35{,}600 \text{ c},$$

and from this the heat of formation of the anhydride can be deduced, namely—

$$(P_2, O_5) = 369{,}900 \text{ c}.$$

Amorphous phosphorus has a smaller heat of oxidation than common phosphorus; but the value varies considerably with the mode of formation of the amorphous modification, so that constant results are not attainable.

6. Oxides and Acids of Arsenic.

(*a*) In its behaviour on neutralization, *arsenic acid* is in complete agreement with phosphoric acid; *arsenious oxide*, on the other hand, in aqueous solution behaves quite differently from phosphorous acid. The trioxide does not combine with water to form an acid, and when dissolved in water shows a basicity with respect to caustic soda which is only half as great as that of phosphorous acid (see p. 102).

Arsenic acid, however, is very notably distinguished from phosphoric acid by its small affinity for water; for the first-mentioned acid is readily converted into the anhydride on heating, whilst phosphoric acid, even on ignition, loses only two-thirds of its hydrogen in the form of water, giving rise to metaphosphoric acid. Arsenic has also a far smaller affinity for oxygen than has phosphorus.

The calorimetric experiments include the heats of formation of both of the oxidation products, as well as the heats of solution of the anhydrides and of arsenic acid. The heats of solution of the anhydrides were derived from the thermal effect produced by their solution in dilute caustic soda, after the known heats of neutralization had been deducted. The heat of solution of arsenic acid, on the other hand, can be measured directly.

The heat of formation of arsenic acid was estimated by means of the reaction between bromine, water, and an excess of finely pulverized arsenic. The bromine is thereby completely converted into hydrobromic acid with the formation of arsenic acid. After the termination of the experiment the amount of hydrobromic acid was quantitatively determined. The heat of reaction for 1 gram-atom of arsenic dissolved is found from the equation—

$$5(H, Br, Aq) - 4(H_2, O) + (H_3, As, O_4, Aq) = 83{,}690 \text{ c},$$

and will therefore be—

$$(H_3, As, O_4, Aq) = 215{,}230 \text{ c}$$
$$(As, O_5, Aq) = 225{,}380.$$

(*b*) *Heat of formation of arsenious oxide. When a very dilute solution of iodic acid is poured into an aqueous solution of arsenious oxide, which contains rather more of the oxide than the amount of iodic acid added is able to oxidize to arsenic acid, the iodic acid is, in the course of a few moments, completely reduced to hydriodic acid.* This process was investigated calorimetrically, and the thermal effect found was equal to 149,975 c for every 2 gram-molecules of iodic acid reduced, consequently—

$$3(As_2O_3Aq,\ O_2) - 2(HIAq,\ O_3) = 149{,}975 \text{ c},$$

whence it follows that—

$$(As_2O_3Aq,\ O_2) = 78{,}410 \text{ c}.$$

Now, since—

$$(As_2,\ O_5,\ Aq) = (As_2,\ O_3,\ Aq) + (As_2O_3Aq,\ O_2),$$

we obtain—

$$(As_2,\ O_3,\ Aq) = 146{,}970 \text{ c}.$$

I also, some years later, measured the *heat of formation of arsenious oxide* in another way; namely, from the thermal effect on decomposition of arsenious chloride with water (see section C on the chlorides of the non-metals). From the heat of decomposition we can deduce the value—

$$(As_2,\ O_3,\ Aq) = 147{,}270 \text{ c},$$

which is in very close agreement with that given above; the mean value 147,120 c will in future be the one adopted.

The determinations of the *heats of solution* of the acids and of the two anhydrides, gave the following results:—

$$(As_2O_3,\ Aq) = -7550 \text{ c}$$
$$(As_2O_5,\ Aq) = +6000$$
$$(H_3AsO_4,\ Aq) = -\ 400$$
$$(As_2O_5,\ 3H_2O) = +6800.$$

From these numbers we arrive at the *heats of formation of the oxides of arsenic in the solid condition*, namely—

$$(As_2,\ O_3) = 154{,}670 \text{ c}$$
$$(As_2,\ O_5) = 219{,}380$$
$$(As_2,\ O_5) - (As_2,\ O_3) = \ 64{,}710$$
$$(H_3,\ As,\ O_4) = 215{,}630.$$

Thus the affinity of arsenic for oxygen is considerably less than that of phosphorus; the difference between (P_2, O_5) and (As_2, O_5) amounts to 150,520 c. It is well known that arsenic anhydride splits up into arsenious oxide and oxygen on ignition, notwithstanding that the decomposition is accompanied by a heat-absorption of 64,710 c.

An aqueous solution of arsenious oxide is known not to be oxidized by iodine, but, on the other hand, immediate oxidation ensues on addition of the hydroxide or carbonate of sodium. The explanation is simple: In the first case we have the reaction—

$$(As_2O_3Aq : I_4) = (As_2O_3Aq,\ O_2) + 4(H,\ I,\ Aq) - 2(H_2,\ O)$$
$$-5630 \text{ c} \quad = \quad 78{,}410 \text{ c} \quad + \quad 52{,}680 \text{ c} \quad - 136{,}720 \text{ c}.$$

The reaction would consequently be attended by a moderately large absorption of heat. If, however, sodium carbonate be added to the aqueous solution of arsenious oxide the conditions are changed, in that the thermal effect is increased by the heat of neutralization of the six molecules of acid formed, which, after deduction of the heat of neutralization of the arsenious acid, produces an additional evolution of 11,422 c. This is far in excess of the amount of energy that is required to decompose the sodium carbonate, and the process therefore results in a considerable evolution of heat.[1]

The difference between the heats of formation of the pentoxide and trioxide of arsenic is one-fifth of the difference between the heats of formation of phosphoric and iodic anhydrides, and is exactly equal to the difference between the heats of formation of sulphuric and selenic acids in the liquid state—

$$(P_2,\ O_5) - (I_2,\ O_5) = 5 \times 64{,}970 \text{ c}$$
$$(As_2,\ O_5) - (As_2,\ O_3) = \quad 64{,}710$$
$$(S,\ O_3,\ H_2O) - (Se,\ O_3,\ H_2O) = \quad 64{,}700.$$

[1] *Note by Translator.*—This is a good instance of a fact to which Ostwald has called attention; namely, that in order that a reaction involving absorption of heat shall take place, any exothermic reaction which can be coupled with it, must be expressible by a single equation. In this instance, it may be taken that the action is due to the formation of a hypoiodite, and its subsequent reaction with the arsenious solution.

This conformity is possibly accidental, but nevertheless it is worthy of note.

7. Oxides of Antimony and Bismuth.

It is not practicable to make a direct estimation of the heats of formation of these oxides, since the products of combustion are not of a constant composition. On the other hand, the heats of formation of the corresponding chlorides can readily be determined by direct methods, and from these the values for the oxides are deduced.

Thus *antimonic acid* is formed from the decomposition of the pentachloride by water; the decomposition is complete, and the hydroxide formed does not contain any chlorine. In the case of the pentachloride I found (see below)

$$(Sb,\ Cl_5) = 104{,}870 \text{ c},$$

whilst the decomposition with water produces the thermal effect—

$$(SbCl_5 : Aq) = 35{,}200 \text{ c},$$

and corresponds to the following reaction :—

$$(SbCl_5 : Aq) = -(SbCl_5) - 3(H_2,\ O) + 5(H,\ Cl,\ Aq) + (H,\ Sb,\ O_3,\ H_2O).$$

By means of the thermal values already given we find that

$$(H,\ Sb,\ O_3,\ H_2O) = 148{,}570 \text{ c},$$

and from this—

$$(Sb_2,\ O_5,\ 3H_2O) = 228{,}780 \text{ c}.$$

On the other hand, the *trichlorides* of antimony and bismuth are not completely decomposed by water; for the corresponding oxides or hydroxides are of a distinctly basic nature, so that they react with some of the hydrochloric acid formed by the decomposition. The compounds resulting from the treatment with cold water have usually, as is well known, the composition $Sb_4O_5Cl_2$ and BiOCl; in which five-sixths of the antimonious chloride and two-thirds of the bismuthous chloride are decomposed. In order to determine the influence which the

formation of these compounds has upon the thermal effect on decomposition of the chlorides with water, the thermal value of the reaction between hydrochloric acid and the hydroxides $Sb(OH)_3$ and $Bi(OH)_3$ was measured under such conditions that compounds of the above-mentioned composition were produced; I found

$$(2SbO_3H_3, HClAq) = 2{,}368 \text{ c}$$
$$(BiO_3H_3, HClAq) = 14{,}180.$$

Thus for every gram-molecule of $SbCl_3$ decomposed, the observed heat of decomposition is 1184 c greater, and for every gram-molecule of $BiCl_3$ 14,180 c greater, than it would have been if the water had completely decomposed the chlorides to hydroxides. The experiments show—

$(SbCl_3 : Aq) = 8910$ c Product: $Sb_4O_5Cl_2$
$(BiCl_3 : Aq) = 7830$ „ $BiOCl.H_2O$,

from which it follows that for a complete decomposition—

$(SbCl_3 : Aq) = 7730$ c Product: $Sb(OH)_3$
$(BiCl_3 : Aq) = -6350$ „ $Bi(OH)_3$.

From the last-mentioned values we can calculate in the usual manner—

$(Sb, O_2, H, H_2O) = 117{,}890$ c | $(Sb_2, O_3, 3H_2O) = 167{,}420$ c
$(Bi, O_2, H, H_2O) = 103{,}050$ | $(Bi_2, O_3, 3H_2O) = 137{,}740$.

A comparison of the heats of formation of antimonious hydroxide and of arsenious oxide shows that *antimony has a greater affinity for oxygen than has arsenic*, and thus we find in the *P*, *As*, and *Sb* group the same relation that was found in the *Cl*, *Br*, and *I*, and in the *S*, *Se*, and *Te* groups, which is, that the *affinity for oxygen is smallest in the middle member of each series, that is to say, for Br, Se, and As respectively.*

8. Compounds of Carbon and Oxygen.

(*a*) *Allotropic modifications* are known to exist in the case of many elements. All the physical properties, such as external appearance, crystalline form, melting-point, specific heat, and

density, and partly also the chemical properties, are altered when an element is converted from one allotropic state into another; at the same time, the amount of energy in the substance also undergoes a change. It has been observed, however, that there appears to be a sort of general rule with regard to some of these changes in property, namely—

When the passage of an element from one allotropic modification to another is attended by an evolution of heat, the newly formed substance will have a greater density and a lower specific heat.

Sulphur, phosphorus, selenium, and carbon form conspicuous examples in this connection, as will be seen from the following numbers :—

State of aggregation.		Density.	Specific heat according to *Regnault*.
Sulphur	monoclinic	1·96	0·1844
	rhombic	2·065	0·1776
Phosphorus	regular	1·83	0·1882
	amorphous	2·10	0·1668
Selenium	amorphous	4·28	0·1031
	crystalline	4·80	0·0760
Carbon	amorphous	2·0	0·114
	diamond	3·5	0·063

In all these instances the transformation takes place with evolution of heat, whence it follows that the heat of combustion is reduced, whilst the density rises and the specific heat becomes less.

(*b*) *Carbon dioxide.*—The heat of combustion of carbon is therefore dependent upon its physical condition; *Favre* and *Silbermann* found that 1 gram-atom, *i.e.* 12 grams, of charcoal on complete combustion produced 96,960 c, whilst the diamond produced only from 93,240 c to 94,540 c, and the heats of combustion of the other modifications of carbon lie somewhere between these values. Under these circumstances I have not thought it necessary to make a determination of the heat of combustion, the more so since the value found would have to be increased by a certain number in order to correspond to

the heat of combustion of a carbon atom in its condition as a constituent of a chemical compound. I shall deal more fully with this subject in a later chapter, under the heading of "Organic Compounds." In the mean time I shall adopt the value found by *Favre* and *Silbermann* as *the heat of combustion of porous carbon* (wood charcoal), namely—

$$(C, O_2) = 96{,}960 \text{ c},$$

and this agrees very closely with the heat of combustion of the carbon formed from purified cellulose, which *Gottlieb* found to be 96,400 c.

I have determined the *heat of absorption* of carbon dioxide as—

$$(CO_2, Aq) = 5880 \text{ c},$$

from which it follows that—

$$(C, O_2, Aq) = 102{,}840 \text{ c}.$$

(*c*) *Carbon monoxide.*—Very special precautions were taken in order to obtain an accurate determination of the heat of combustion of carbon monoxide, since this value, similarly to the heat of formation of water and of hydrogen chloride, enters into the calculations connected with a number of reactions. Two series of experiments, comprising in all ten combustions, and carried out with an intervening interval of two years, and with different calorimeters, gave precisely the same result, namely—

$$(CO, O) = 67{,}960 \text{ c at constant pressure.}$$

In the course of the experiments 33·3 litres in all of carbon monoxide were burned. If now we subtract the number found from the heat of combustion of carbon we obtain the *heat of formation of carbon monoxide.*

$$(C, O) = \begin{cases} 29{,}000 \text{ c at constant pressure} \\ 29{,}290 \text{ c } \quad \text{,,} \quad \text{,,} \quad \text{volume.} \end{cases}$$

With respect to the numerous experimental details the reader is referred to *Therm. Unters.*, vol. ii. p. 284, *et seq.*

(*d*) The heat of formation of *oxalic acid* was derived from the thermal effect on oxidation of an aqueous solution with

hypochlorous acid, when carbonic and hydrochloric acids are formed. For experimental details see reference above. The result is—

$$(C_2O_3Aq, O) = 62{,}000 \text{ c},$$

which is the thermal value for the oxidation of a solution of oxalic acid to *gaseous* carbon dioxide by means of oxygen. And since the heat of formation of this oxide is taken as 96,960 c, we therefore obtain—

$$(C_2, O_3, Aq) = 131{,}920 \text{ c}$$
$$(C_2, O_4, H_2, Aq) = 200{,}280.$$

I have found the *heats of solution* of crystalline and of anhydrous oxalic acid to be—

$$(C_2H_2O_4 . 2H_2O, Aq) = -8588 \text{ c crystalline acid}$$
$$(C_2H_2O_4, Aq) = -2256 \quad \text{anhydrous acid.}$$

Thus two gram-molecules of water are taken up by the anhydrous acid $C_2H_2O_4$ with an evolution of 6332 c.

The heat of formation of the anhydrous acid is therefore

$$(C_2, H_2, O_4) = 202{,}540 \text{ c},$$

and for the *crystallized acid*

$$(C_2, H_2, O_4, 2H_2O) = 208{,}870 \text{ c}.$$

Oxalic acid forms a connecting link between the monoxide and dioxide of carbon; this is best seen by a comparison of the heats of formation of the acids in aqueous solution, taking carbon monoxide as the starting-point; we then have—

$(2CO, O, Aq) = 1 \times 73{,}920$ c Product : C_2O_3Aq
$(2CO, O_2 Aq) = 2 \times 73{,}840$,, $2CO_2Aq$

that is to say, the *evolution of heat is proportional to the amount of oxygen*. This is another example of the fact that the thermal values of analogous processes can be regarded as multiples of a common magnitude.

C. Chlorides and Oxychlorides of the Non-metals.

A large number of these compounds can be formed by direct methods, and their heats of formation can therefore also be measured directly. This holds good for the compounds of

chlorine with iodine, sulphur, selenium, tellurium, phosphorus, arsenic, antimony, and bismuth; whilst the determination of the heats of formation of the chlorides of carbon requires a special mode of treatment. The heats of formation of the oxychlorides, on the other hand, are most easily derived from their decomposition by water, when hydrogen chloride and the corresponding acid are formed.

1. Monochloride and Trichloride of Iodine.

Iodine monochloride, ICl, was formed directly in the calorimeter from iodine crystals and gaseous chlorine. The product, as is well known, is a liquid. *Iodine trichloride*, ICl_3, on the other hand, is formed by passing chlorine into iodine monochloride. The result was as follows:—

$(I_2, Cl_2) = 11{,}650$ c Product: liquid ICl
$(ICl, Cl_2) = 15{,}660$ } „ solid ICl_3.
$(I, Cl_3) = 21{,}490$ }

Thus the thermal effect resulting from combinations between these analogous substances is by no means small.

2. Sulphur, Selenium, and Tellurium.

The monochlorides of sulphur and selenium were formed directly in the calorimeter; the thermal values, after taking into account the fact that sulphur and selenium were dissolved by the product of the reaction, amounted to—

$(S_2, Cl_2) = 14{,}257$ c
$(Se_2, Cl_2) = 22{,}150$.

The tetrachlorides of selenium and tellurium were also formed in the calorimeter, the first by the action of chlorine upon selenium monochloride, the second directly from tellurium and chlorine. The result was—

$(Se, Cl_4) = 46{,}156$ c
$(Te, Cl_4) = 77{,}377$.

A comparison of these values with those above shows that the *affinity between these substances and chlorine rises considerably from sulphur to selenium and tellurium.*

I have also investigated the thermal effect on decomposition of the tetrachlorides of selenium and tellurium, and found—

$(SeCl_4 : Aq) = 30{,}370$ c
$(TeCl_4 : Aq) = 20{,}345$
} Decomposition by solution in water.

We have seen above (p. 215) that these numbers can he utilized for the calculation of the heats of formation of selenious and tellurous acids.

3. Phosphorus, Arsenic, Antimony, and Bismuth.

(*a*) *Phosphorus.*—Since the heats of formation of phosphorous and phosphoric acids are already known, the heats of formation of PCl_3, PCl_5, and $POCl_3$ can easily be calculated from the thermal effect due to their decomposition by water. For these three reactions I found—

$(PCl_3 : Aq) = 65{,}140$ c
$(PCl_5 : Aq) = 123{,}440$
$(POCl_3 : Aq) = 72{,}191$
} Decomposition by solution in water.

As an example we have—

$$(PCl_3 : Aq) = (H_3, P, O_3, Aq) + 3(H, Cl, Aq) - (P, Cl_3) - 3(H_2O)$$
$$65{,}140 \text{ c} = 227{,}570 \text{ c} + 117{,}945 \text{ c} - (P, Cl_3) - 205{,}080 \text{ c}.$$

This equation gives us the heat of formation of PCl_3, and in a similar manner those of the other compounds can be found, namely—

$(P, Cl_3) = 75{,}300$ c
$(P, Cl_5) = 104{,}990$
$(PCl_3, Cl_2) = 29{,}690$
$(PCl_3, O) = 70{,}660$
$(P, Cl_3, O) = 145{,}960.$

Thus we see that the heat of formation of the oxychloride from the trichloride and oxygen is far greater than that on

formation of the pentachloride from the trichloride and chlorine.

In order to obtain a control value for these numbers, I made a direct measurement of the thermal effect due to the combination of the trichloride with chlorine, and found 29,692 c, which is in complete agreement with the calculated difference between the thermal values for the penta- and trichlorides.

(*b*) *Arsenic.*—The heat of formation of arsenious chloride is measured directly; by the action of chlorine upon metallic arsenic the thermal value is 71,463 c. Since the heat of oxidation of arsenious oxide has already been determined, the heat of formation of the trichloride can also be calculated from the thermal effect due to its decomposition by water. For this reaction I found 17,583 c, and we thus arrive at 71,307 c as the heat of formation of the trichloride, which agrees exactly with the value found by direct measurement. We therefore have the following values for arsenic :—

$$(As,\ Cl_3) = 71{,}390\ \text{c}$$
$$(As,\ Cl_3 : Aq) = 17{,}580.$$

(*c*) *Antimony and bismuth.*—The heats of formation of the trichlorides were also in this case measured directly; that of antimony pentachloride, on the other hand, was found by taking the sum of the heat of formation of the trichloride and of the thermal change resulting from the action of chlorine upon the trichloride. The result was—

$$(Sb,\ Cl_3) = 91{,}390\ \text{c}$$
$$(SbCl_3,\ Cl_2) = 13{,}480$$
$$(Sb,\ Cl_5) = 104{,}870$$
$$(Bi,\ Cl_3) = 90{,}630.$$

The trichlorides of antimony and bismuth are known to be only partially decomposed by cold water, the respective products being $Sb_4O_5Cl_2$ and BiOCl.

The thermal effects as measured were—

$(SbCl_3 : Aq) = 8910$ c Product : $Sb_4O_5Cl_2$
$(BiCl_3 : Aq) = 7830$ BiOCl . H_2O.

This gives us the heat of formation of *bismuth oxychloride*,

$$(Bi, O, Cl, H_2O) = 88{,}180 \text{ c},$$

and the thermal effect of the action of hydrochloric acid on bismuth hydroxide,

$$(BiO_3H_3, HClAq) = 14{,}180 \text{ c},$$

a value which shows the strongly basic character of bismuth hydroxide. On complete hydrolysis of the chlorides by water the thermal effect would be—

$(SbCl_3 : Aq) = +\ 7730$ c Product : $Sb(OH)_3$
$(BiCl_3 : Aq) = -\ 6350$ „ $Bi(OH)_3$.

The decomposition of *antimony pentachloride* by water was found to be

$$(SbCl_5 : Aq) = 35{,}200 \quad \text{Product : } SbO_4H_3.$$

Thus phosphorus, arsenic, atimony, and bismuth show the following affinities for chlorine :—

R	(R, Cl_3)	(R, Cl_5)	$(R, Cl_5) - (R, Cl_3)$
P	75,300 c	104,990 c	29,690
As	71,390	—	—
Sb	91,390	104,870	13,480
Bi	90,630	—	—

We see that in the case of the trichlorides the affinity of chlorine for antimony and bismuth is far greater than for phosphorus and arsenic ; but the pentachlorides of phosphorus and antimony have equal heats of formation. It follows from this that the last two atoms of chlorine are more feebly bound in antimony pentachloride than they are in phosphorus pentachloride. This explains the use of antimony pentachloride as a powerful chlorinating agent for organic compounds.

4. Compounds of Carbon and Chlorine.

(*a*) None of the usual calorimetric methods are adapted to the determination of the affinity of carbon for chlorine; partly because such compounds as CCl_4, C_2Cl_4, etc., cannot be formed directly from their elements, partly because they are not spontaneously combustible in oxygen, and finally because they are not decomposed in aqueous solution in such a manner as to enable us to utilize the heats of reaction for the calculation of the values required.

I therefore adopted the following method for the determination of the heats of formation of the chlorides of carbon: *The gas, or compound in the form of vapour, was mixed with hydrogen and burnt in oxygen.* Theoretically the method is very simple, but in practice a number of difficulties are encountered. Suitable apparatus is required, as well as specially careful manipulation, *so that when all the necessary precautions are taken these experiments may certainly be regarded as amongst the most difficult and tedious in the study of thermochemistry.*

For all particulars concerning the apparatus employed, the method of working, and the calculation of the observed results, the reader is referred to the very detailed description in *Therm. Unters.*, vol. ii. 339–358.

A large number of carbon compounds containing chlorine will be referred to in the chapter on the heats of formation of organic substances; here I shall give only the results of the researches on carbon tetrachloride, tetrachlorethylene, and carbonyl chloride, which most closely resemble the compounds of the non-metals already described.

(*b*) *Carbon tetrachloride*, CCl_4.—The experimental result was as follows: *When a gram-atom of charcoal, in that modification which has a heat of combustion equal to* 96,960 *c*, *combines with* 2 *gram-molecules of chlorine, and the product is supposed to be in the state of vapour at a temperature of* 19°, *the combination is attended by a heat-evolution of* 21,030 *c*.

This result is of great interest; *partly* because it shows the very powerful affinity between carbon and chlorine, although

they do not unite directly; *partly as evidence that the heats of formation of carbon tetrachloride and of methane are very nearly equal.* We thus have for the gaseous products—

$$(C, H_4) = 21{,}750\,c$$
$$(C, Cl_4) = 21{,}030.$$

This equality of the two thermal values affords an important contribution towards the elucidation of several chlorinating and reduction processes of organic substances which will be discussed later on.

(*c*) *Tetrachlorethylene*, C_2Cl_4.—Experiments with tetrachlorethylene show that the union of 2 gram-atoms of carbon with 2 gram-molecules of chlorine to form C_2Cl_4 in the state of vapour of normal density at 19° takes place with an *absorption* of 1150 c. Here, again, there is a marked similarity between the affinities of chlorine and hydrogen for carbon, since the heat of formation of ethylene is also negative. The values are—

$$(C_2, H_4) = -2710\,c$$
$$(C_2, Cl_4) = -1150.$$

(*d*) *Carbonyl chloride.*—This compound was formed directly from chlorine and carbon monoxide under the influence of light. To purify the substance it was condensed in a cooling mixture, the condensed liquid was distilled in a suitable apparatus, and the vapour collected over mercury in a gas-holder of about 3-litre capacity. In a pure, dry state, the gas does not act upon mercury, or at least not within the time required for the performance of the experiment. Indiarubber, on the other hand, is very strongly attacked, so that only glass connections must be employed in carrying out the investigations.

Carbonyl chloride is only very slowly decomposed by water, but more quickly by a solution of caustic potash. The carbon dioxide formed is not, however, completely dissolved unless very strong potash is used, and it was therefore necessary, on analyzing the solution, to determine not only the amount of hydrochloric acid formed, but also that of the carbon dioxide absorbed, so as to make the requisite correction in the calculation for the carbon dioxide which escaped absorption. On

the complete decomposition of 1 gram-molecule of $COCl_2$, and the absorption of the whole of the gas formed, there is a heat-evolution of 105,175 c, from which we calculate in the usual manner that the heat of formation of carbonyl chloride is 55,620 c.

To control the accuracy of these numbers, a second series of determinations was carried out, in which carbonyl chloride mixed with hydrogen was burned in oxygen in precisely the same manner as in the preceding experiments with CCl_4 and C_2Cl_4. According to these experiments the heat of formation of carbonyl chloride should be 54,650 c, whilst the decomposition with potassium hydroxide gave the value 55,620 c. We can therefore put the *heat of formation of carbonyl chloride at*

$$(C, O, Cl_2) = 55{,}140\,c.$$

Since the heat of formation of carbon monoxide is 29,000 c, we obtain—

$$(CO, Cl_2) = 26{,}140\,c,$$

and this high thermal value explains the direct formation of carbonyl chloride from carbon monoxide and chlorine.

D. Compounds of Carbon with Sulphur and Nitrogen.

1. *Carbon disulphide*, CS_2.—The heat of formation of carbon disulphide is deduced from the heat of combustion of the substance in oxygen. Together with the dioxides of carbon and sulphur there is always formed a small amount of sulphur trioxide, so that in the calorimetric experiments the products of the combustion must be quantitatively analyzed. Carbon disulphide in the form of vapour is passed into the calorimeter, and from the measured thermal effect the *heat of combustion of the gaseous substance at* 20° can be calculated. Assuming the combustion to be normal, that is to say, that the products are exclusively composed of the dioxides of carbon and sulphur, we find that

$$(CS_2 : O_6) = 265{,}130\,c.$$

From this we calculate in the usual manner that the *heat of formation of* 1 *gram-molecule of* CS_2 *in the gaseous state is*

$$(C, S_2) = -26{,}010 \text{ c for gaseous } CS_2 \text{ at } 20°.$$

Since the heat of vaporization of 1 gram-molecule of carbon disulphide is 6400 c, the heat of formation will consequently be

$$(C, S_2) = -19{,}610 \text{ c for liquid } CS_2.$$

The heat of formation is in all cases negative; but this arises from the large amount of energy with which the carbon must be supplied in order to bring about the conditions under which it enters into its compounds. I shall deal with this subject in a later chapter on the heat of formation of organic substances. Carbon is known to unite directly with sulphur, but only at a high temperature; and this is also the case when carbon combines with oxygen and with hydrogen.

2. *Carbonyl sulphide.*—This compound was formed directly from carbon monoxide and sulphur vapour, which combine with ease when they are led together through a tube filled with pumice and warmed. The compound was purified by treatment with alcoholic potash, when it is converted into ethylmonothiocarbonate of potassium, which, after crystallization from absolute alcohol, was decomposed with hydrogen chloride. The product was washed with water at 0°, dried, and collected in a gasometer over mercury. On combustion in oxygen it, similarly to carbon disulphide, forms a little sulphur trioxide, the amount of which must of course be determined. *The heat of combustion* was found to be

$$(COS : O_3) = 131{,}010 \text{ c.}$$

This is almost exactly half of the heat of combustion of 1 gram-molecule of CS_2, for which we found 265,130 c. From the heat of combustion we can, in the usual manner, find the *heat of formation of* 1 *gram-molecule of COS*, namely—

$$(C, O, S) = 37{,}030 \text{ c,}$$

from which, finally, we can deduce the thermal effect on

formation of carbonyl sulphide from carbon monoxide and sulphur, namely—

$$(CO, S) = 8030 \text{ c.}$$

These values apply to rhombic sulphur and amorphous carbon.

It is worthy of note that the heat of formation of carbonyl sulphide lies about midway between the heats of formation of carbon dioxide and of carbon disulphide, and similarly that that of carbonyl chloride lies about midway between those of carbon dioxide and of carbon tetrachloride. Thus we have—

$$\begin{array}{llll} (O, C, O) = & 96{,}960 \text{ c} & (O, C, O) & = 96{,}960 \text{ c} \\ (S, C, O) = & 37{,}030 & (Cl_2, C, O) & = 55{,}140 \\ (S, C, S) = & -26{,}010 & (Cl_2, C, Cl_2) & = 21{,}030. \end{array}$$

In the first case the mean value is 35,475 c; in the second, 58,995 c. The explanation of this difference may possibly be that a reaction takes place within the unsymmetrical molecule, between sulphur and oxygen in the one case, and between chlorine and oxygen in the other; the former gives rise to an increased heat of formation, the latter, on the contrary, to a lower.

3. *Cyanogen and hydrogen cyanide.*—The heats of formation of these two carbon compounds are derived from their heats of combustion, which are respectively 259,620 c and 158,620 c (see Part IV.). Calculating in the usual manner we find

$$\begin{aligned} (C_2, N_2) &= -65{,}700 \text{ c} \\ (H, C, N) &= -27{,}480. \end{aligned}$$

The heats of formation are therefore strongly negative, which is due to the amount of energy which must be supplied to the carbon in order to bring about the condition under which it enters into chemical compounds. On the other hand, *cyanogen and hydrogen combine with evolution of heat.* From the numbers above we calculate that

$$(C_2N_2 : H_2) = 2(H, C, N) - (C_2, N_2) = 10{,}740 \text{ c.}$$

Thus the heat evolved is about one-quarter of that observed in the action of 1 gram-molecule of chlorine upon 1 gram-molecule of hydrogen (namely, 44,000 c).

In Chapter IX. which follows will be found tabulated the numerical results of the whole of my researches on combinations between the non-metals.

CHAPTER IX

COMPOUNDS OF THE NON-METALS. COMPARATIVE TABLES OF THE NUMERICAL RESULTS

THE following tables contain the results of researches on compounds of the non-metals arranged in the manner most convenient for reference. The substances are arranged in groups in the order of their valency, so that each group contains all the values connected with that particular non-metal. But in order to avoid repetition, the arrangement is, as a rule, based upon the electro-positive non-metal of the compound. So that, for example, all the compounds of sulphur, whether they contain oxygen, hydrogen, or chlorine, will be found under the group sulphur, similarly the oxygen, hydrogen, chlorine, and sulphur compounds of carbon are placed in the carbon group.

All the thermal values quoted apply to reactions of the constituents at a *temperature* of from 18° to 20° C., and at *constant pressure*. Unless anything to the contrary is stated, the *state of aggregation* is always that in which the substance occurs under normal conditions at the temperature specified; so that bromine and water are referred to as liquids, iodine, sulphur, and phosphorus, on the other hand, as solids.

In the formulæ employed the reactions are always supposed to take place between those constituents which are separated by a comma (,) or by a colon (:), and in those proportions which are represented by the formula. The comma usually indicates that the constituents enter into direct combination; the colon, on the contrary, that they decompose one another. The sign *Aq* in the formulæ represents a large amount of water, and consequently indicates that the reaction in question is

supposed to take place in solution; thus (*HCl, Aq*) signifies the heat of absorption of gaseous hydrogen chloride, but (*H, Cl, Aq*) expresses the formation of an aqueous solution of hydrochloric acid from the constituents hydrogen, chlorine, and water.

The *atomic weights* used for the non-metals will be found on page 45, and the thermal value expresses the number of heat units—that is to say, that amount of heat required to raise unit weight of water at 18° through 1° C.—corresponding to that weight of the reacting substances which the formula represents.

TABLE 18.

Thermal Effect on Formation of Compounds of the Non-metals.

(*a*) *Hydrogen and Hydrogen Peroxide.*

Reaction.	Thermal effect.	Remarks.
(*Cl, H*)	22,000 c	The thermal effect is valid for the reaction at constant pressure, and for the constituents and products in their normal state of aggregation at 18°.
(*Br, H*)	8,440	
(*I, H*)	− 6,040	
(*O, H_2*)	+68,360	
(*S, H_2*)	2,730	
(*N, H_3*)	11,890	The heat of fusion of 1 gram-molecule of H_2O, according to *Regnault*, is 1440 c, and the heat of vaporization is 9660 c at 100°.
(*C, H_4*)	21,750	
(*C_2, H_6*)	28,560	
(*C_2, H_4*)	− 2,710	
(*C_2, H_2*)	−47,770	
(*C_6, H_6*)	− 5,310	Valid for liquid benzene.
	−12,510	,, benzene vapour at 18°.
(*Cl, H*)	21,984 + 0·9 *t*	Valid at temperature *t*, when both the constituents and the products formed are assumed to be in the state of gas or vapour.
[*Br, H*]	11,704 + 0·9 *t*	
[*I, H*]	−605 + 0·9 *t*	
[*O, H_2*]	57,903 + 1·6 *t*	
[*S, H_2*]	4,435 + 1·9 *t*	
(*N, H_3*)	11,792 + 5·0 *t*	

Hydrogen Peroxide.

(*H_2, O_2, Aq*)	45,300 c	Formation and decomposition of hydrogen peroxide in aqueous solution.
(*H_2O, O, Aq*)	−23,060	
(*H_2O_2Aq, H_2*)	−91,420	

(*b*) *Oxygen.*

Reaction.	Thermal effect.	Remarks.
(H_2, O)	68,360 c	Product : liquid.
(Cl_2, O)	−17,930	,, gaseous.
(N_2, O)	−17,470	,, ,,
(N, O)	−21,575	,, ,,
(C, O)	+29,000	For amorphous carbon.
(C, O_2)	96,960	,, ,, (Favre).
(S, O_2)	71,080	Product : gaseous.
(Se, O_2)	57,080	,, crystalline.
(N, O_2)	− 8,125	,, NO_2 completely dissociated.
(N_2, O_4)	− 2,650	,, N_2O_4 non-dissociated.
(S, O_3)	103,240	,, liquid.
(As_2, O_3)	154,670	,, solid.
(I_2, O_5)	45,030	,, ,,
(As_2, O_5)	219,380	,, ,,

(*c*) *Chlorine.*

1. General Summary.

(H, Cl)	22,000 c	Of these compounds, HCl and Cl_2O are gases ; ICl_3, $SeCl_4$, $TeCl_4$, PCl_5, $SbCl_3$, and $BiCl_3$ are solids ; and the remaining compounds are liquids at 18° to 20°. The thermal values are valid for the substances in their normal state of aggregation at this temperature, and for rhombic sulphur, amorphous selenium, metallic tellurium, regular phosphorus, and amorphous carbon.
(I, Cl)	5,830	
(I, Cl_3)	21,490	
(O, Cl_2)	−17,930	
(S_2, Cl_2)	+14,260	
(Se_2, Cl_2)	22,150	
(Se, Cl_4)	46,160	
(Te, Cl_4)	77,380	
(P, Cl_3)	75,300	
(P, Cl_5)	104,990	
(As, Cl_3)	71,380	
(Sb, Cl_3)	91,390	
(Sb, Cl_5)	104,870	
(Bi, Cl_3)	90,630	
(C, Cl_4)	28,230	Product : liquid.
	21,030	,, gaseous.
(C_2, Cl_4)	6,000	,, liquid.
	− 1,150	,, gaseous.

2. Hydrochloric Acid, HCl.

(H, Cl)	22,000 c	Product : gaseous.
(H, Cl, Aq)	39,315	,, aqueous solution.
(HCl, Aq)	17,315	Heat of absorption.
$(NaOHAq, HClAq)$	13,780	,, neutralization.

Reaction.	Thermal effect.	Remarks.

3. Hypochlorous Acid, HClO.

(Cl_2, O)	−17,930 c	Product : gaseous.
(Cl_2, O, Aq)	− 8,490	,, aqueous solution.
(Cl_2O, Aq)	+ 9,440	Heat of absorption.
(H, Cl, O, Aq)	29,930	Product : HClOAq.
$(NaOHAq, HClOAq)$	9,980	Heat of neutralization.

4. Chloric Acid, $HClO_3$.

(Cl_2, O_5, Aq)	−20,480 c	Product : Cl_2O_5Aq.
(H, Cl, O_3, Aq)	+23,940	,, $HClO_3Aq$.
$(HClOAq, O_2)$	− 5,990	Formation of $HClO_3$ by oxidation of HClOAq or HClAq.
$(HClAq, O_3)$	−15,380	
$(KOHAq, HClO_3Aq)$	+13,760	Heat of neutralization.

5. Potassium Chlorate, $KClO_3$.

(K, Cl, O_3)	95,860 c	$KClO_3$ formed from the elements and by oxidation of KCl.
(KCl, O_3)	− 9,750	
$(KClO_3, Aq)$	−10,040	Heat of solution.
(K, Cl, O_3, Aq)	+85,820	Aqueous solution.
$(KClOAq, O_2)$	− 2,210	Oxidation of KClO or KCl in aqueous solution.
$(KClAq, O_3)$	−15,370	

6. Oxidation Constants.

$2(H, Cl, Aq) - (H_2, O)$	10,270 c	Oxidation by chlorine and water.
$(H,Cl,Aq) - (H,Cl,O,Aq)$	9,380	,, HCl and HClO.
$(H,ClAq) - (H,Cl,O_3Aq)$	15,380	,, HCl and $HClO_3$.
(Cl_2, Aq)	4,870	Heat of absorption.

(*d*) *Bromine.*

1. Hydrobromic Acid, HBr.

(H, Br)	8,440 c	Gaseous HBr formed from liquid bromine.
(H, Br, Aq)	28,380	Solution of HBr
(HBr, Aq)	19,940	Heat of absorption.
$(NaOHAq, HBrAq)$	13,750	Heat of neutralization.

2. Hypobromous Acid, HBrO.

(Br_2, O, Aq)	−14,993 c	Product : aqueous solution.
(H, Br, O, Aq)	+26,682	

3. Bromic Acid, $HBrO_3$.

(Br_2, O_5, Aq)	−43,520 c	Product : aqueous solution.
(H, Br, O_3, Aq)	+12,420	
$(HBrAq, O_3)$	−15,960	Oxidation of HBrAq.
$(NaOHAq, HBrO_3Aq)$	13,780	Heat of neutralization.

Reaction.	Thermal effect.	Remarks.
	4. Potassium Bromate, $KBrO_3$.	
(K, Br, O_3)	84,060 c	Product: cryst. $KBrO_3$.
(KBr, O_3)	−11,250	Product: cryst. $KBrO_3$.
$(KBrO_3, Aq)$	− 9,760	Heat of solution.
(K, Br, O_3, Aq)	+74,300	Formation in aqueous solution.
$(KBrAq, O_3)$	−15,930	Oxidation of a solution of KBr.
	5. Oxidation Constants.	
$2(H, Br, Aq) - (H_2, O)$	−11,600 c	Oxidation with bromine and water.
$2(H, BrAq) - (H_2, O)$	−12,680	,, bromine water.
(Br_2, Aq)	+ 1,080	Heat of solution.
$(Br_2 gas, Aq)$	+ 7,643	Absorption of bromine gas.
$(Br_2 gas) - (Br_2 liq.)$	+ 6,560	Difference in energy content at 19°.
	(e) Iodine.	
	1. Hydriodic Acid, HI.	
(H, I)	− 6,040 c	Product: gaseous.
(H, I, Aq)	+13,170	,, aqueous solution.
(HI, Aq)	19,210	Heat of absorption.
$(NaOHAq, HIAq)$	13,680	,, neutralization.
	2. Iodic Acid, HIO_3.	
(I_2, O_5)	45,030 c	Product: I_2O_5.
(H, I, O_3)	57,960	,, HIO_3.
(I_2, O_5, H_2O)	47,570	,, $2HIO_3$.
(I_2, O_5, Aq)	43,240	,, aqueous solution.
(H, I, O_3, Aq)	55,800	,, aqueous solution.
(I_2O_5, H_2O)	2,540	Heat of hydration.
(I_2O_5, Aq)	− 1,790	Heat of solution.
(HIO_3, Aq)	− 2,170	Heat of solution.
$(HIAq, O_3)$	+42,630	Oxidation of HIAq to HIO_3Aq.
(HI, O_3)	64,000	Oxidation of gaseous HI to solid HIO_3.
	3. Potassium Iodate, KIO_3.	
(K, I, O_3)	124,490 c	Product: solid.
(KI, O_3)	44,360	Product: solid.
(KIO_3, Aq)	− 6,780	Heat of solution.
(K, I, O_3, Aq)	117,710	Product: aqueous solution.
$(KIAq, O_3)$	42,690	Product: aqueous solution.
$(KOHAq, HIO_3Aq)$	13,810	Heat of neutralization.
	4. Periodic Acid, H_5IO_6.	
(H_5, I, O_6)	185,780 c	Product: crystalline.
(H_5, I, O_6, Aq)	184,400	,, aqueous solution.
(H_5IO_6, Aq)	− 1,380	Heat of solution.
(I_2, O_7, Aq)	27,000	Product: aqueous solution.
(H, I, O_4, Aq)	47,680	Product: aqueous solution.
$(HIAq, O_4)$	34,510	Oxidation of HI solution.
$(KOHAq, H_5IO_6Aq)$	5,150	Heat of neutralization (see p. 104).
$(2KOHAq, H_5IO_6Aq)$	26,590	Heat of neutralization (see p. 104).

Reaction.	Thermal effect.	Remarks.
5. Chlorides of Iodine, ICl and ICl_3.		
(I, Cl)	5,830 c	Product: liquid ICl.
(I, Cl_3)	21,490	,, solid ICl_3.
(ICl, Cl_2)	15,660	,, ,, ICl_3
$(I_2 gas) - (I_2 solid)$	10,900	Difference in energy content at 19°.
(*f*) *Sulphur, Rhombic.*		
1. Hydrogen Sulphide, H_2S.		
(H_2, S)	2730 c	Product: gaseous.
(H_2, S, Aq)	7290	,, aqueous solution.
(H_2S, Aq)	4560	Heat of absorption.
2. Sulphur Dioxide, SO_2.		
(S, O_2)	71,080 c	For monoclinic sulphur 71,720 c.
$[S, O_2]$	77,280	Product: liquid SO_2.
(S, O_2, Aq)	78,780	,, aqueous solution.
$(SO_2 gas) - (SO_2 liq.)$	6,200	Heat of liquefaction at 19°.
(SO_2, Aq)	7,700	,, absorption.
$[SO_2, Aq]$	1,500	Solution of liquid SO_2 in water.
$(2NaOHAq, SO_2Aq)$	28,970	Heat of neutralization.
3. Sulphuric Acid, H_2SO_4.		
(S, O_3)	103,240 c	Product: liquid anhydride.
(SO_2, O)	32,160	Oxidation of SO_2 to SO_3.
(H_2, S_2, O_7)	298,860	Product: liquid $H_2S_2O_7$.
$(2SO_3, H_2O)$	24,020	Heat of hydration.
(H_2, S, O_4)	192,920	Formation of liquid H_2SO_4 from the constituents specified.
(S, O_3, H_2O)	124,560	
(SO_3, H_2O)	21,320	
(SO_2, O, H_2O)	53,480	
(H_2, SO_2, O_2)	121,840	
(S, O_3, Aq)	142,410	Formation of a solution of sulphuric acid from the constituents specified.
(SO_2, O, Aq)	71,330	
(SO_2Aq, O)	63,630	
(H_2, S, O_4, Aq)	210,770	
(SO_2, Aq)	39,170	Heat of solution of the anhydride and acids in 1600 mol. H_2O.
$(H_2S_2O_7, Aq)$	54,320	
(H_2SO_4, Aq)	17,850	
$(2NaOHAq, SO_3Aq)$	31,380	Heat of neutralization.
4. Thiosulphuric Acid, $H_2S_2O_3$.		
(S_2, O_2, Aq)	69,470 c	Formation in aqueous solution.
(H_2, S_2, O_3, Aq)	137,830	
(SO_2, S, Aq)	− 1,610	Formation from sulphurous acid and sulphur.
(SO_2Aq, S)	− 9,310	
$(Na_2, S_2, O_3, 5H_2O)$	265,070	Product: $Na_2S_2O_3 + 5H_2O$.

Reaction.	Thermal effect.	Remarks.
	5. Dithionic Acid, $H_2S_2O_6$.	
(S_2, O_5, Aq)	211,080 c	Formation of aqueous solution.
(H_2, S_2, O_6, Aq)	279,440	
$(2SO_2, O, Aq)$	68,920	Formation by oxidation of SO_2 or SO_2Aq.
$(2SO_2Aq, O)$	53,520	
(SO_3Aq, SO_2Aq)	− 10,110	From sulphuric and sulphurous acids.
(K_2SO_4, SO_2)	0	
(K_2, S_2, O_6)	415,720	Product : solid $K_2S_2O_6$.
$(K_2S_2O_6, Aq)$	− 13,010	Heat of solution.
$(2KOHAq, S_2O_5Aq)$	+ 27,070	,, neutralization.
	6. Tetrathionic Acid, $H_2S_4O_6$.	
(S_4, O_5, Aq)	192,430 c	Formation in aqueous solution.
(H_2, S_4, O_6, Aq)	260,790	
$(H_2S_2O_6Aq, S_2)$	− 18,650	From dithionic acid and sulphur.
$(2H_2S_2O_3Aq, O)$	53,490	By oxidation of thiosulphuric acid.
	7. Sulphur Chloride and Sulphuryl Chloride.	
(S_2, Cl_2)	14,260 c	Direct formation.
(S_2Cl_2, S_2)	− 1,660	Solution of S in S_2Cl_2.
(S, O_2, Cl_2)	89,780	Formation from the elements.
(SO_2, Cl_2)	18,700	,, ,, SO_2 and Cl_2.

(*g*) *Selenium, Amorphous.*

	1. Chlorides of Selenium, S_2Cl_2 and $SeCl_4$.	
(Se_2, Cl_2)	22,150 c	Direct formation.
(Se, Cl_4)	46,160	
$(Se_2Cl_2, 3Cl_2)$	70,170	Product : $2SeCl_4$.
$(SeCl_4 : Aq)$	30,370	Heat of solution.
	2. Selenious Acid, SeO_2.	
(Se, O_2)	57,080 c	Product : cryst. SeO_2.
(Se, O_2, Aq)	56,160	,, aqueous solution.
(SeO_2, Aq)	− 920	Heat of solution.
(Na_2OAq, SeO_2Aq)	27,020	,, neutralization.
	3. Selenic Acid, H_2SeO_4.	
(Se, O_3, Aq)	76,660 c	Direct formation in solution.
(SeO_2, O, Aq)	19,580	Oxidation of SeO_2 and SeO_2Aq.
(SeO_2Aq, O)	20,500	
(H_2, Se, O_4, Aq)	145,020	Product : H_2SeO_4Aq.
(H_2SeO_4, Aq)	16,800	Heat of solution of liquid H_2SeO_4 (Metzner).
(H_2, Se, O_4)	128,220	Product : liquid H_2SeO_4.
(Se, O_3, H_2O)	59,860	
(Na_2OAq, SeO_3Aq)	30,390	Heat of neutralization.

(*h*) *Tellurium, Metallic.*

Reaction.	Thermal effect.	Remarks.
	1. Telluric Chloride, $TeCl_4$.	
(Te, Cl_4)	77,380 c	Direct formation.
$(TeCl_4 : Aq)$	20,340	Heat of solution.
	2. Tellurous Acid, H_2TlO_3.	
(Te, O_2, H_2O)	77,180 c	From tellurium, oxygen, and water.
	3. Telluric Acid, H_2TlO_4.	
(Te, O_3, Aq)	98,380 c	Direct formation in solution.
(H_2TeO_3, O, Aq)	21,200	By oxidation of tellurous acid.

(*j*) *Nitrogen.*

	1. Ammonia, NH_3.	
(N, H_3)	11,890	Direct formation.
(N, H_3, Aq)	20,320	,, ,, in solution.
(NH_3, Aq)	8,430	Heat of absorption.
(NH_3, HCl)	41,900	Cryst. compounds: *e.g.* NH_4Cl formed from the gaseous constituents NH_3 and HCl.
(NH_3, HBr)	45,020	
(NH_3, HI)	43,460	
(NH_3, HSH)	22,440	
(N, H_4, Cl)	75,790	Formation of salts from their elements.
(N, H_4, Br)	65,350	
(N, H_4, I)	49,310	
(N, H_5, S)	37,060	
(N_2, H_4, O_2)	64,950	
(N_2, H_4, O_3)	88,060	
$(NH_3Aq, HClAq)$	12,270	Heat of neutralization.
$(NH_3Aq, HSHAq)$	6,190	
	2. Hydroxylamine, NOH_3.	
(N, H_3, O, Aq)	24,290 c	Direct formation in solution.
(NH_3Aq, O)	3,970	By oxidation of NH_3Aq.
(N, O, H_4, Cl)	76,510	Product: $NOH_3 . HCl$.
(NOH_4Cl, Aq)	− 3,650	Heat of solution.
$(N_2O_2H_6 . H_2SO_4, Aq)$	− 960	
$(NOH_3Aq, HClAq)$	+ 9,260	,, neutralization.
$(2NOH_3Aq, SO_3Aq)$	21,580	
	3. Nitrous Oxide, N_2O.	
(N_2, O)	−17,470 c	Direct formation.
(NO, N)	+ 3,885	Formation from NO and N.
$(N_2O, 2H_2O)$	−30,930	Product: NH_4NO_3.

Reaction.	Thermal effect.	Remarks.
	4. Nitric Oxide, NO.	
(N, O)	−21,575 c	Direct formation.
$(N_2O : O)$	−25,410	Product : 2NO.
	5. Nitrous Acid, HNO_2.	
(N_2, O_3, Aq)	− 6,820 c	Direct formation in solution.
(H, N, O_2, Aq)	+30,770	Direct formation in solution.
$(2NO_2, O, Aq)$	+36,330	Formation from NO.
(H, NO, O, Aq)	+52,345	Formation from NO.
$(N_2, 2H_2O)$	+71,770	Product : NH_4NO_2.
	6. Nitrogen Dioxide, NO_2.	
(N, O_2)	− 8,125 c	Product *completely* dissociated.
(NO, O)	+13,450	Product *completely* dissociated.
	7. Nitrogen Tetroxide, N_2O_4.	
(N_2, O_4)	− 2,650 c	Heat of formation *without* dissociation of N_2O_4.
$(2NO, O_2)$	+40,500	Heat of formation *without* dissociation of N_2O_4.
(N_2O_4, Aq)	14,150	Heat of absorption.
(NO_2, NO_2)	13,600	N_2O_4 formed from $2NO_2$.
	8. Nitric Acid, NHO_3.	
(H, N, O_3)	41,610 c	Direct formation, product liquid.
(H, N, O_3, Aq)	49,090	,, ,, in solution.
(HNO_3, Aq)	7,480	Heat of solution.
(HNO_2Aq, O)	18,320	By oxidation of a solution of HNO_2.
(H, NO, O_2, Aq)	70,665	Formation of a solution of nitric acid from NO, NO_2, and N_2O_4 respectively.
(H, NO_2, O, Aq)	57,215	Formation of a solution of nitric acid from NO, NO_2, and N_2O_4 respectively.
(H_2, N_2O_4, O_2, Aq)	100,830	Formation of a solution of nitric acid from NO, NO_2, and N_2O_4 respectively.
(H, NO, O_2)	63,185	Formation of nitric acid from NO, NO_2, and N_2O_4 respectively.
(H, NO_2, O)	49,735	Formation of nitric acid from NO, NO_2, and N_2O_4 respectively.
(H_2, N_2O_4, O_2)	85,870	Formation of nitric acid from NO, NO_2, and N_2O_4 respectively.
(N_2, O_5, Aq)	29,820	Formation of N_2O_5Aq from N_2, N_2O, 2NO, $2NO_2$, and N_2O_4 respectively.
(N_2O, O_4, Aq)	47,560	Formation of N_2O_5Aq from N_2, N_2O, 2NO, $2NO_2$, and N_2O_4 respectively.
$(2NO, O_3, Aq)$	72,970	Formation of N_2O_5Aq from N_2, N_2O, 2NO, $2NO_2$, and N_2O_4 respectively.
$(2NO_2, O, Aq)$	46,070	Formation of N_2O_5Aq from N_2, N_2O, 2NO, $2NO_2$, and N_2O_4 respectively.
(N_2O_4, O, Aq)	32,470	Formation of N_2O_5Aq from N_2, N_2O, 2NO, $2NO_2$, and N_2O_4 respectively.
$(NaOHAq, HNO_3Aq)$	13,680	Heat of neutralization.
	9. Cyanogen and Hydrogen Cyanide, C_2N_2 and HCN.	
(C_2, N_2)	−65,700 c	Product : gaseous.
$(H, C, N)_{gas}$	−27,480	Product : gaseous.
$(H_2 : C_2N_2)$	+10,740	,, 2HCN.
(HCN, Aq)	6,100	Heat of absorption.
(H, C, N, Aq)	−21,380	
$(NaOHAq, HCNAq)$	+ 2,770	,, neutralization.

(*k*) *Phosphorus, Regular.*

Reaction.	Thermal effect.	Remarks.
1. Chlorides and Oxychlorides.		
(P, Cl_3)	75,300 c	Direct formation from the elements.
(P, Cl_5)	104,990	
(P, Cl_3, O)	145,960	
(PCl_3, Cl_2)	29,690	PCl_5 and $POCl_3$ formed from PCl_3.
(PCl_3, O)	70,660	
$(PCl_3 : Aq)$	65,140	Heat of solution.
$(PCl_5 : Aq)$	123,440	
$(POCl_3 : Aq)$	72,190	
2. Hypophosphorous Acid, H_3PO_2.		
(H_3, P, O_2)	139,970 c	Cryst. acid.
	137,660	Liquid acid.
(H_3, P, O_2, Aq)	139,800	Aqueous solution.
(H_3PO_2, Aq)	− 170	Heat of solution of the cryst. acid.
	+2,140	,, ,, liquid ,,
$(P_2, O, 3H_2O)$	74,860	Product : cryst. acid.
(P_2, O, Aq)	74,520	,, aqueous solution.
$(NaOH, H_3PO_2Aq)$	15,160	Heat of neutralization.
3. Phosphorous Acid, H_3PO_3.		
(H_3, P, O_3)	227,700 c	Cryst. acid.
	224,630	Liquid acid.
(H_3, P, O_3, Aq)	227,570	Aqueous solution.
(H_3PO_3, Aq)	− 130	Heat of solution of the cryst. acid.
	+2,940	,, ,, liquid ,,
$(P_2, O_3, 3H_2O)$	250,320	Product : cryst. acid.
(P_2, O_3, Aq)	250,060	,, aqueous solution.
$(2NaOH, H_3PO_3Aq)$	28,450	Heat of neutralization.
4. Phosphoric Acid, H_3PO_4.		
(H_3, P, O_4)	302,600 c	Cryst. acid.
	300,080	Liquid acid.
(H_3, P, O_4, Aq)	305,290	Aqueous solution.
(H_3PO_4, Aq)	2,690	Heat of solution of the cryst. acid.
	5,210	,, ,, liquid ,,
(P_2, O_5)	369,900	Anhydride.
$(P_2, O_5, 3H_2O)$	400,120	Cryst. acid.
(P_2, O_5, Aq)	405,500	Aqueous solution.
$(3NaOH, H_3PO_4Aq)$	34,030	Heat of neutralization.

(*l*) *Arsenic.*

1. Arsenious Chloride, $AsCl_3$.		
(As, Cl_3)	71,390 c	Direct formation.
$(AsCl_3 : Aq)$	17,580	Heat of solution.

Reaction.	Thermal effect.	Remarks.
2. Arsenious Oxide, As_2O_3.		
(As_2, O_3)	154,670 c	Anhydride.
(As_2, O_3, Aq)	147,120	Aqueous solution.
(As_2O_3, Aq)	− 7,550	Heat of solution.
(Na_2OAq, As_2O_3Aq)	+13,780	,, neutralization.
3. Arsenic Acid, H_3AsO_4.		
(As_2, O_5)	219,380 c	Anhydride.
$(As_2, O_5, 3H_2O)$	226,180	Hydrate.
$(As_2O_5, 3H_2O)$	6,800	Heat of hydration.
(As_2, O_5, Aq)	225,380	Aqueous solution.
(H_3, As, O_4)	215,630	Cryst. acid.
(As_2O_3, O_2)	64,710	By oxidation of As_2O_3 and As_2O_3Aq to arsenic acid.
(As_2O_3Aq, O_2)	78,260	
(As_2O_5, Aq)	6,000	Heat of solution.
(H_3AsO_4, Aq)	− 400	
$(3NaOH, H_3AsO_4Aq)$	+35,920	,, neutralization.

(*m*) *Antimony.*

1. Chlorides.

(Sb, Cl_3)	91,390 c	Direct formation.
(Sb, Cl_5)	104,870	
$(SbCl_3, Cl_2)$	13,480	$SbCl_5$ formed from $SbCl_3$ and Cl_2.
$(SbCl_3 : Aq)$	7,730	On complete decomposition.
	8,910	On formation of $Sb_4O_5Cl_2$.
$(SbCl_5 : Aq)$	35,200	On complete decomposition.

2. Antimonious Acid, $HSbO_2 + H_2O$.

$(Sb_2, O_3, 3H_2O)$	167,420 c	Product : $2Sb(OH)_3$.
(H, Sb, O_2, H_2O)	117,890	,, $Sb(OH)_3$.

3. Antimonic Acid, $HSbO_3 + H_2O$.

$(Sb_2, O_5, 3H_2O)$	228,780 c	Product : $2H_3SbO_4$.
(H, Sb, O_3, H_2O)	148,570	,, H_3SbO_4.
(SbO_3H_3, O)	30,680	Oxidation of $Sb(OH)_3$ to H_3SbO_4.

(*n*) *Bismuth.*

Chlorides and Oxychlorides, $BiCl_3$ and $BiOCl$.

(Bi, Cl_3)	90,630 c	Product : $BiCl_3$.
(Bi, O, Cl, H_2O)	88,180	,, $BiOCl . H_2O$.
$(BiCl_3 : H_2O, Aq)$	7,830	,, $BiOCl . H_2O$.
$(BiCl_3 : 3H_2O, Aq)$	− 6,350	,, $Bi(OH)_3$.
$(BiO_3H_3, HClAq)$	+14,180	,, $BiOCl . H_2O$.

Reaction.	Thermal effect.	Remarks.
Bismuth Hydroxide, $Bi(OH)_3$.		
$(Bi_2, O_3, 3H_2O)$	137,740 c	Product: $2Bi(OH)_3$.
(H, Bi, O_2, H_2O)	103,050	,, $Bi(OH)_3$.

(*o*) *Carbon, Amorphous.*

1. Hydrocarbons.

Reaction.	Thermal effect for *gaseous* products at constant pressure.	Thermal effect for *gaseous* products at constant volume.	Remarks.
(C, H_4)	21,750 c	21,170 c	Methane.
(C_2, H_6)	28,560	27,400	Ethane.
(C_2, H_4)	− 2,710	− 3,290	Ethylene.
(C_2, H_2)	−47,770	−47,770	Acetylene.
(C_6, H_6)	−12,510	−13,670	(for liq. benzene − 5310 c).
(C_2H_2, H_2)	+45,060	+44,480	Product: C_2H_4.
(C_2H_4, H_2)	31,270	30,690	,, C_2H_6.
$(C_2H_6 : H_2)$	14,940	14,940	,, $2CH_4$.

2. Chlorides.

(C, Cl_4)	21,030 c	20,450 c	(for liquid CCl_4 : 28,230 c).
(C_2, Cl_4)	− 1,150	− 1,730	(,, C_2Cl_4 : 6,000 c).
$(C_2Cl_4 : 2Cl_2)$	+43,210	+42,630	Product: $2CCl_4$.
$(CCl_4 : 4H_2)$	88,720	88,720	,, $CH_4 + 4HCl$.
$(CH_2 : 4Cl_2)$	87,280	87,280	,, $CCl_4 + 4HCl$.

3. Oxides and Sulphur Compounds.

(C, O)	29,000 c	29,290 c	Direct formation from amorphous carbon (*Favre*)
(C, O_2)	96,960	96,960	
(C, S_2)	−26,010	−25,430	For liquid CS_2 : − 19,610 c.
(C, O, S)	+37,030	37,320	Product: COS.
(C, O, Cl_2)	55,140	54,850	,, $COCl_2$.
(CO, O)	67,960	67,670	,, CO_2.
(CO, S)	8,030	8,030	,, COS.
(CO, Cl_2)	26,140	25,560	,, $COCl_2$.

4. Oxalic Acid, $C_2H_2O_4$.

Reaction.	Thermal effect at constant pressure.	Remarks.
(C_2, O_4, H_2)	202,540 c	Product: anhydrous acid.
$(C_2, O_4, H_2, 2H_2O)$	208,870	,, crystalline ,,
$(C_2O_4H_2, 2H_2O)$	6,330	Heat of hydration.
$(C_2O_4H_2, Aq)$	−2,260	,, solution.
$(C_2O_4H_2 . 2H_2O, Aq)$	−8,590	,, solution.
$(2CO, O, Aq)$	73,920	Product: $C_2H_2O_4Aq$.

5. Carbon Dioxide, CO_2.

(C, O_2)	96,960 c	Amorphous carbon (*Favre*).
(CO_2, Aq)	5,880	Heat of absorption.
(C, O_2, Aq)	102,840	Product: CO_2Aq.
(CO, O, Aq)	73,840	Product: CO_2Aq.

The thermal effect on formation of the more complex carbon compounds, commonly called organic, will be described in Part IV., which is specially devoted to these substances.

PART III

COMPOUNDS OF METALS WITH NON-METALS

CHAPTER X

COMPOUNDS OF METALS: OXIDES, HYDROXIDES, HALIDES, SALTS, SULPHIDES, ETC.

AMONGST the numerous values published in the preceding chapters will be found numerical data which can be utilized in calculating the heats of formation of compounds of the metals; such as the thermal effect on formation of acids from their elements, the heats of neutralization of a large number of acids and bases, the heats of hydration and of solution of salts and halogen compounds, etc. All that remains therefore is to determine the thermal effect for some reaction into which the metal enters as such, in order to obtain the necessary data for the calculation of the heats of formation of its compounds.

A direct measure of the heat of formation of a compound of a metal from its elements can but rarely be accomplished with the requisite accuracy. We are therefore compelled, as a rule, to derive the value from the thermal effects of a series of processes in which the compounds in question are formed or decomposed by indirect methods. Thus the heats of oxidation of the alkali metals are calculated from the thermal effect of their action on water; for other metals the estimation is based upon the thermal effect of their solution in acids, or on that of the precipitation of the metal from one of its compounds, etc.

The subject-matter of Part III. is arranged as follows: Chapter X. contains an account of the methods adopted in the case of each of the metals in order to determine the necessary

factor for the calculation of the heats of formation of its compounds. Next, in Chapter XI., will be found a list of the heats of formation of the more important compounds of the metals arranged in systematic order; and finally, in the last chapter, we review the affinity relationships of the different substances from the dynamical standpoint.

A. Lithium, Sodium, and Potassium.

The alkali metals decompose water at ordinary temperatures, and the determination of the heats of formation of their compounds can be based upon this process. The reaction is very vigorous, being least so for lithium and greatest for potassium, and special measures must be devised to moderate the violence of the reaction (see *Therm. Unters.*, vol. iii. pp. 222–237).

The process comprises the decomposition of water with evolution of hydrogen and the formation of an aqueous solution of the hydroxide of the metal. The thermal effect is calculated from the equation

$$V = (R, O, H, Aq) - (H_2, O).$$

The amount of metal employed was determined by titrating the solution formed by means of a solution of hydrochloric acid, the titer of which corresponded to $AgNO_3 = 170$ gr. Thus the determination was independent of the atomic weights adopted for these metals.

In the table below will be found the experimental results, as well as the calculated heats of formation of the alkaline hydroxides in aqueous solution :—

R	$(R, O, H, Aq) - (H_2, O)$	(R, O, H, Aq)
Li	49,080 c	117,440 c
Na	43,450	111,810
K	48,100	116,460

The numbers in column 3 are obtained by adding the heat of formation of water, *i.e.* 68,360 c, to the thermal values found experimentally.

The heats of solution of the hydroxides of sodium and potassium were determined by direct methods to be

$$(NaOH, Aq) = 9940 \text{ c}$$
$$(KOH, Aq) = 13{,}290 \text{ c.}$$

From these values and those previously given we can now calculate the heats of formation of a large number of the compounds of these metals. To take an example.

The heat of formation of sodium chloride is to be found from the equations—

$$\left.\begin{matrix} 111{,}810 \text{ c} \\ 39{,}315 \\ 13{,}745 \end{matrix}\right| \begin{matrix} (Na, O, H, Aq) \\ +(H, Cl, Aq) \\ +(NaOHAq, HClAq) \end{matrix} \Bigg\} = \left\{\begin{matrix} (Na, Cl, Aq) \\ +(H_2, O) \end{matrix}\right| \begin{matrix} x \\ 68{,}360 \text{ c} \end{matrix}$$

whence it follows that—

$$x = (Na, Cl, Aq) = 96{,}510 \text{ c};$$

that is to say, we assume that aqueous solutions of sodium hydroxide and of hydrochloric acid are first formed from the elements Na, O, H_2, and Cl, together with water, and that these solutions subsequently neutralize each other. The total thermal effect is then equal to that which would result from the formation of water and an aqueous solution of sodium chloride from the same elements (cf. page 9).

Now, since

$$(Na, Cl) + (NaCl, Aq) = (Na, Cl, Aq)$$
$$(Na, Cl) - 1180 \text{ c} = 96{,}510 \text{ c}$$

we obtain

$$(Na,Cl) = 97{,}690 \text{ c},$$

that is, *the heat of formation of* 1 *gram-molecule of NaCl* from its elements at 18° C.

In a similar manner the heats of formation of other compounds can be calculated. The values so found for the more important compounds of the alkali metals are given in the tables in Chapter XI.

B. Aluminium and Magnesium.

These metals dissolve readily in a dilute solution of hydrochloric acid with evolution of hydrogen. In the experiments an acid of concentration $HCl + 200H_2O$ was employed, and the thermal values were

$$(Al_2 : 6HClAq) = 239{,}760 \text{ c}$$
$$(Mg : 2HClAq) = 108{,}290.$$

So that we find, for example, for aluminium

$$(Al_2 : 6HClAq) = (Al_2, Cl_6, Aq) - 6(H, Cl, Aq)$$
$$239{,}760 \text{ c} = (Al_2, Cl_6, Aq) - 235{,}890 \text{ c},$$

whence it follows that—

$$(Al_2, Cl_2, Aq) = 475{,}650 \text{ c},$$

and since, according to Table I., page 50, the heat of solution of the chloride in water amounts to

$$(Al_2Cl_6, Aq) = 153{,}690 \text{ c},$$

the *heat of formation of anhydrous, crystalline aluminium chloride* will be

$$(Al_2, Cl_6) = 321{,}960 \text{ c}.$$

From the heat of reaction of $(Al_2 : 6HClAq)$ we can then deduce the *heat of formation of aluminium hydroxide* in the following manner :—

$$(Al_2 : 6HClAq) = (Al_2, O_3, 3H_2O) + (Al_2O_6H_6, 6HClAq) - 3(H_2, O),$$

and since the heat of neutralization of aluminium hydroxide is 55,920 c, we obtain

$$(Al_2, O_3, 3H_2O) = 388{,}920 \text{ c}.$$

In the same manner, in the case of magnesium we find

$$(Mg, Cl_2) = 151{,}010 \text{ c}$$
$$(Mg, O, H_2O) = 148{,}960 \text{ c}.$$

For the remaining values, see the tables in Chapter XI.

C. Calcium, Strontium, and Barium.

The oxides of these metals have a very strong affinity for water, in which, like the corresponding hydroxides, they are soluble. Since the heats of neutralization of aqueous solutions of the bases have already been given, we can determine the heats of hydration of the oxides, together with the heats of solution both of the oxides and hydroxides, by measuring the thermal effect due to their solution in hydrochloric acid ($HCl + 200H_2O$). The results were as follows :—

Reaction	$R = Ca$	$R = Sr$	$R = Ba$
$(RO, 2HClAq)$	46,030 c	56,970 c	62,300 c
$(RO_2H_2, 2HClAq)$	30,490	39,270	40,040
$(RO_2H_2 . 8H_2O, 2HClAq)$	—	12,990	12,570
$(RO_2H_2Aq, 2HClAq)$	27,700 [1]	27,630	27,780

from which on subtraction we can find the *heats of hydration*

(RO, H_2O)	15,540 c	17,700 c	22,260 c
$(RO_2H_2, 8H_2O)$	—	26,280	27,470

and the *heats of solution*

(RO, Aq)	+18,330 c	+29,340 c	+34,520 c
(RO_2H_2, Aq)	+ 2,790	+11,640	+12,260
$(RO_2H_2 . 8H_2O, Aq)$	—	−14,640	−15,210

The table shows that the heat of solution of the oxide (RO, Aq), as well as the thermal effect on formation of the first hydrate (RO, H_2O), rises appreciably from calcium to barium; or, in other words, that *the affinity for water is greatest for baryta and least for lime*—that is to say, it is greatest for the more readily soluble substance.

The heats of oxidation of the metals can, of course, be determined by the method employed in the case of the preceding metals, since the alkaline earths decompose water and dilute hydrochloric acid solutions at ordinary temperatures.

[1] Direct experiment with lime-water gave 27,900 c.

The difficulty in obtaining accurate results arises from our not being able to procure the metals in a sufficiently pure state. Moisson, however, appears to have succeeded in preparing pure calcium by heating calcium iodide with sodium, and he also, at the same time, took the opportunity of determining the heat of oxidation; the value he found was

$$(Ca,O) = 145{,}000 \text{ c},$$

and I have therefore made use of this number in calculating the heats of formation of the remaining calcium compounds (see the following tables) instead of the value that I myself had found about thirty years previously for electrolytic calcium. M. Guntz has only recently succeeded in preparing barium in a pure state, and, as a consequence, the heat of oxidation has not been accurately settled. The present experimental value is 104,000 c, but this is certainly too low, since in the method previously employed for the preparation of barium, namely, from the amalgam, it always contained a little mercury.

Strontium, on the other hand, can be electrolytically deposited in a tolerably pure condition, and in this case I found

$$(Sr : 2HClAq) = 117{,}050 \text{ c},$$

from which is derived in the usual manner—

$$(Sr, O) = 128{,}440 \text{ c}.$$

The amount of metal dissolved was determined by measuring the volume of hydrogen evolved during the reaction, and is thus independent of the small trace of chloride—derived from the solution in which the metal was electrolyzed—which may possibly be enclosed within its pores. The heats of formation of the remaining compounds are to be found in the tables.

D. Manganese, Zinc, Cadmium, Nickel, and Cobalt.

The calculation of the thermal effects on formation of the compounds of these metals is also based upon the heat evolved on solution of the metal in hydrochloric acid of the necessary

concentration. The values found, calculated for an acid of composition $HCl + 200H_2O$, were as follows :—

R	$(R : 2HClAq)$
Mn	49,370 c
Zn	34,210
Cd	17,610
Fe	21,320
Ni	16,190
Co	15,070

From these numbers we can, in the manner already described, derive the heats of formation of the chlorides RCl_2, of the hydroxides $R(OH)_2$, and of other compounds. These values are given in the tables. With respect to the heats of formation of the higher oxides, we note—

1. *Manganese.*—From the foregoing heat of reaction on solution of manganese in hydrochloric acid we obtain for the corresponding hydroxide—

$$(Mn, O, H_2O) = 94,770 \text{ c.}$$

Now, it was found, on investigating oxidation and reduction processes (*Therm. Unters.*, vol. ii. pp. 445–467), that the thermal effect on oxidation of this substance to manganic hydroxide amounted to

$$(MnO_2H_2, O) = 21,560 \text{ c},$$

and on addition of these two values we find the heat of formation of *manganic hydroxide*, namely—

$$(Mn, O_2, H_2O) = 116,330 \text{ c.}$$

In a similar manner I determined the thermal effect on oxidation of manganous hydroxide to permanganic acid in alkaline solution,

$$(2MnO_2H_2, O_5, 2KOHAq) = 14,760 \text{ c},$$

and from this we can calculate the heat of formation of *permanganic acid* itself: we find

$$(2MnO_2H_2, O_5, Aq) = -12,740 \text{ c.}$$

This negative value shows that the oxygen taken up is very weakly bound.

If now we add to the preceding number, namely 14,760 c, the heat of formation of 2 gram-molecules of $Mn(OH)_2$ or $2 \times 94{,}770$ c, we obtain

$$(Mn_2,\ O_7,\ 2KOHAq) = 204{,}300 \text{ c},$$

and from this again we can calculate the heat of formation of *potassium permanganate* from its elements $(K_2,\ Mn_2,\ O_8)$: namely

$$\begin{array}{c|c|c|c} x & \{(K_2,\ Mn_2,\ O_8)+ & \{(K_2,\ O,\ Aq)+ & 164{,}560 \text{ c} \\ -20{,}790 & \{(K_2Mn_2O_8,\ Aq)\} = & \{(Mn_2,\ O_7,\ 2KOHAq) & 204{,}300. \end{array}$$

From which it follows that—

$$x = (K_2,\ Mn_2,\ O_8) = 389{,}650 \text{ c}.$$

In a similar manner the heats of formation of the other compounds can be calculated.

2. *Iron.*—Iron forms two series of compounds, ferrous and ferric chloride, ferrous and ferric oxide, etc. From the heat of solution of iron in hydrochloric acid (*i.e.* 21,320 c) we find in the usual manner—

$$(Fe,\ Cl_2,\ Aq) = 99{,}950 \text{ c}.$$

Now, since the thermal effect of the action of chlorine upon a solution of ferrous chloride is

$$(2FeCl_2Aq,\ Cl_2) = 55{,}540 \text{ c},$$

a value which has been determined with great accuracy, and for which concordant results have been obtained by three methods (*Therm. Unters.*, ii. 453), we obtain on addition—

$$(Fe_2,\ Cl_6,\ Aq) = 255{,}440 \text{ c}.$$

Moreover, since the heats of solution of the chlorides are known (see page 51), namely—

$$\begin{aligned} (FeCl_2,\ Aq) &= 17{,}900 \text{ c} \\ (Fe_2Cl_6,\ Aq) &= 63{,}360, \end{aligned}$$

we obtain by subtraction—

$$\begin{aligned} (Fe,\ Cl_2) &= 82{,}050 \text{ c} \\ (Fe_2,\ Cl_6) &= 192{,}080. \end{aligned}$$

In a similar manner the *heats of formation of the hydroxides* can be found: for these we find

$$(Fe, O, H_2O) = 68{,}280 \text{ c}$$
$$(Fe_2, O_3, 3H_2O) = 191{,}150.$$

It is noteworthy that the last four numbers are *multiples of a common factor*, namely—

$$(Fe, Cl_2) = 82{,}050 \text{ c} = 6 \times 13{,}675 \text{ c}$$
$$(Fe_2, Cl_6) = 192{,}080 = 14 \times 13{,}720$$
$$(Fe, O, H_2O) = 68{,}280 = 5 \times 13{,}656$$
$$(Fe_2, O_3, 3H_2O) = 191{,}150 = 14 \times 13{,}654.$$

A similar relation has been observed for the chloride and hydroxide of aluminium, namely—

$$(Al_2, Cl_6) = 321{,}960 \text{ c} = 24 \times 13{,}415 \text{ c}$$
$$(Al_2, O_3, 3H_2O) = 388{,}920 = 29 \times 13{,}411.$$

Likewise the values for the chlorides and hydroxides of other metals are in multiple proportion, as will be seen from the table below:—

R	(R, O, H_2O)	(R, Cl_2)
Mg	11 × 13,542 c	11 × 13,728 c
Mn	7 × 13,539	8 × 13,998
Zn	6 × 13,780	7 × 13,887
Fe	5 × 13,646	6 × 13,675

It can, therefore, scarcely be regarded as a chance relationship when the thermal values of so large a number of processes prove to be multiples of a constant magnitude.

3. *Cobalt and nickel*, similarly to manganese and iron, form higher oxides. To determine the heats of formation of the corresponding hydroxides, solutions of the metallic chloride, RCl_2, were precipitated by the addition of a strongly alkaline solution of sodium hypochlorite, and the resulting thermal effect was measured. In this manner a black precipitate of the higher hydroxide is obtained; the proportionate amount of oxygen being estimated in each experiment. Two series of experiments were carried out for every metal; in the one case, 1

gram-molecule of NaOCl reacted with 2 gram-molecules of RCl_2; in the other, there was double the amount of sodium hypochlorite, so that the NaOCl and RCl_2 were in equivalent quantities. In the first case the hydroxide precipitated contained 2·99 atoms of oxygen to 2 atoms of cobalt, in the second there were 3·346 atoms of oxygen to 2 atoms of cobalt. We can thus, in the manner described in *Therm. Unters.*, vol. iii. pp. 298–303, calculate the heat of reaction on oxidation of cobaltous to cobaltic hydroxide, and it is found that—

$$(2CoO_2H_2,\ O,\ H_2O) = 22{,}580 \text{ c.}$$

Oxidation is therefore attended by a tolerably strong evolution of heat when $2CoO \cdot H_2O$ is converted into $Co_2O_3 \cdot H_2O$. On the other hand, in the second group of experiments it is evident that a further oxidation does not produce any increased evolution of heat. For whilst the first gram-atom of oxygen, as already stated, gives rise to 22,580 c, the thermal effect on addition of 1·346 gram-atoms of oxygen is only 22,370 c; so that it would appear that the further oxidation to *hydrated cobalt peroxide*, $CoO_2 + H_2O$, is attended by a small negative thermal effect.

Experiments with *nickel* show a somewhat different behaviour. Even with an excess of sodium hypochlorite the oxidation does not proceed beyond the formation of the *sesquioxide*, and this oxidation is accompanied by a negative effect, namely—

$$(2NiO_2H_2,\ O,\ H_2O) = -1300 \text{ c.}$$

Iron, cobalt, and nickel form a small group of metals with atomic weights lying between 56 and 59, and of which the affinity towards oxygen changes throughout the series in the manner demonstrated in the following table :—

R	(R, O, H_2O)	$(2RO_2H_2, O, H_2O)$	$(R_2, O_3, 3H_2O)$
Fe	68,280 c	54,590 c	191,150 c
Co	63,400	22,580	149,300
Ni	60,840	−1,300	120,380

There is, therefore, some justification for the assumption that the succession in the periodic system should be Fe, Co, Ni, and not, as is generally supposed, Fe, Ni, Co.

4. *Cadmium.*—The heat of formation of cadmium hydroxide, cadmium chloride, and other compounds can be derived in the usual manner from the thermal effect on solution of the metal in hydrochloric acid; thus we find

$$(Cd, O, H_2O) = 65{,}680 \text{ c}$$
$$(Cd, Cl_2) = 93{,}240, \text{ etc.}$$

But cadmium, however, exhibits an anomaly which must be taken into account in calculating the heats of formation of the other halides. For whilst hydrochloric, hydrobromic, and hydriodic acids usually produce an exactly equal evolution of heat on neutralization by the same base, such as the hydroxides of zinc, magnesium, copper, barium, sodium, etc., this is not the case when the base is cadmium hydroxide, notwithstanding that its three halides are all soluble in water. For it is then found that the heat of neutralization rises very appreciably, proceeding from hydrochloric to hydrobromic and hydriodic acids. I have thoroughly investigated this peculiarity with the following result:—

$$(CdO_2H_2, 2HClAq) = 20{,}290 \text{ c}$$
$$(CdO_2H_2, 2HBrAq) = 21{,}560$$
$$(CdO_2H_2, 2HIAq) = 24{,}210.$$

A comparison with the heats of neutralization found for the hydroxides of zinc, magnesium, and copper is given in the table below:—

	$Zn(OH)_2$	$Mg(OH)_2$	$Cu(OH)_2$	$Cd(OH_2)$
2HClAq	19,483 c	27,313 c	14,602 c	20,295 c
2HBrAq	19,647	—	14,748	21,561
2HIAq	19,606	27,312	—	24,208

This irregularity must be taken into consideration in

calculating the heats of formation of the chloride, bromide, and iodide of cadmium, when we find that—

$$(Cd, Cl_2) = 93{,}240 \text{ c}$$
$$(Cd, Br_2) = 75{,}200$$
$$(Cd, I_2) = 48{,}830.$$

E. Copper.

Copper forms two well-known oxides, Cu_2O and CuO; and the calculation of the heats of formation of the two corresponding series of compounds is based upon the thermal effect due to the formation of these oxides.

Copper does not dissolve in dilute hydrochloric acid, and, as a consequence, the mode of procedure adopted in the case of the metals already described is not applicable. On the other hand, a solution of copper sulphate is decomposed by metallic iron, and the thermal effect of this process was therefore measured. The experimental result was as follows :—

$$(CuSO_4Aq : Fe) = 37{,}240 \text{ c},$$

which is, of course, the difference between the heats of formation of the sulphates of iron and copper in aqueous solution, so that we have—

$$(Fe, O, SO_3Aq) - (Cu, O, SO_3Aq) = 37{,}240 \text{ c}$$
$$(Fe, O, SO_3Aq) = 93{,}200 \quad \text{(see Table 29)}$$
$$(Cu, O, SO_3Aq) = 55{,}960 \text{ c}.$$

Now, since the thermal effect on solution of CuO in dilute sulphuric acid is 18,800 c (see p. 120), we obtain *the heat of formation of cupric oxide*—

$$(Cu, O) = 37{,}160 \text{ c},$$

and from this we can calculate in the usual manner the heats of formation of the other cupric compounds, for instance for *cupric chloride*—

$$(Cu, O) + 2(H, Cl, Aq) + (CuO, 2HClAq) = (Cu, Cl_2, Aq) + (H_2, O)$$
$$37{,}160 \text{ c} + 78{,}640 \text{ c} + 15{,}270 \text{ c} = (Cu, Cl_2, Aq) + 68{,}360 \text{ c},$$

so that

$$(Cu, Cl_2, Aq) = 62{,}710 \text{ c};$$

and since the heat of solution of anhydrous copper chloride is 11,080 c (see p. 52), we find by subtraction

$$(Cu, Cl_2) = 51{,}630 \text{ c}.$$

In order to determine the heat of formation of *cuprous oxide*, Cu_2O, and the corresponding halides, six series of experiments were carried out. In three of these, solutions of hydrochloric, hydrobromic, and hydriodic acids were decomposed by means of cuprous oxide, when water and the respective insoluble cuprous halides were formed. The thermal values in the three cases were

$$(Cu_2O, 2HClAq) = 14{,}660 \text{ c}$$
$$(Cu_2O, 2HBrAq) = 20{,}760$$
$$(Cu_2O, 2HIAq) = 33{,}730.$$

The second group of experiments comprised a determination of the thermal effect on decomposition of cuprous oxide by means of dilute sulphuric acid, metallic copper and a solution of cupric sulphate being formed. The result was

$$(Cu_2O : SO_3Aq) = (CuO, SO_3Aq) - (CuO, Cu) = 15{,}160 \text{ c},$$

and since

$$(CuO, Cu) = (Cu_2, O) - (Cu, O),$$

it follows, from the number found on p. 268, that the *heat of formation of cuprous oxide* is 40,800 c.

This value was finally controlled by two other determinations, namely, by the thermal effect of the reaction between cuprous chloride, potassium permanganate, and an aqueous solution of hydrochloric acid, in which cupric chloride is formed, and by that of the formation of cuprous iodide by the action of copper sulphate upon potassium iodide and aqueous sulphurous acid. The heat of formation of cuprous oxide can be calculated from the thermal values of both of these processes, and taking the average of the separate measurements we obtain a probable mean value of 40,810 c for the three sets of experiments, thus—

$$(Cu_2, O) = 40{,}810 \text{ c}.$$

By means of this number we can now find the heats of formation of *cuprous chloride, bromide, and iodide*—

$$(Cu_2, Cl_2) = 65{,}750 \text{ c}$$
$$(Cu_2, Br_2) = 49{,}970$$
$$(Cu_2, I_2) = 32{,}520.$$

The remaining calorimetric constants for copper will be found in the tables.

F. Tin.

Tin forms two characteristic series of compounds, corresponding to the chlorides $SnCl_4$ and $SnCl_2$. The heat of formation of *stannous chloride* is derived from the thermal effect on precipitation of an aqueous, or a very dilute hydrochloric acid, solution of stannous chloride by means of metallic zinc, when zinc chloride and metallic tin are formed; the thermal value is

$$(SnCl_2Aq : Zn) = 31{,}700 \text{ c},$$

whence it follows that—

$$(Sn, Cl_2, Aq) = 81{,}140 \text{ c}.$$

Finally, the thermal effect of the action of chlorine upon a solution of stannous chloride was determined; this amounts (*Therm. Unters.*, ii. 443) to

$$(SnCl_2Aq, Cl_2) = 76{,}030 \text{ c},$$

from which it follows that—

$$(Sn, Cl_2, Aq) + (SnCl_2Aq, Cl_2) = (Sn, Cl_4, Aq) = 157{,}170 \text{ c}.$$

Now, since the heats of formation of these chlorides are (see p. 52)

$$(SnCl_2, Aq) = 350 \text{ c}$$
$$(SnCl_4, Aq) = 29{,}920,$$

it follows, by subtraction from the thermal values given above, that the *heat of formation of the chlorides* in the anhydrous state is

$$(Sn, Cl_2) = 80{,}790 \text{ c}$$
$$(Sn, Cl_4) = 127{,}250.$$

The affinity between tin and chlorine is thus very considerable.

The chlorides are so completely hydrolyzed on dissolving in water that the solution, on neutralization with caustic soda, gives almost the same thermal value as free hydrochloric acid. Calculating for the *reaction between hydrochloric acid and the hydroxides corresponding to these oxides*, we find

$$(SnO_2H_2,\ 2HClAq) = 2770 \text{ c}$$
$$(SnO_4H_4,\ 4HClAq) = 3110.$$

Both hydroxides are soluble in caustic soda solution, and I found the following heats of reaction :—

$$(SnO_2H_2,\ 3NaOHAq) = 215 \text{ c}$$
$$(SnO_4H_4,\ 4NaOHAq) = 9560,$$

and, as we should expect, the thermal effect is greatest for stannic hydroxide.

A solution of stannic chloride in water is precipitated by a solution of sodium sulphate, a property which has a practical application in the quantitative estimation of tin. The thermal effect is in this case negative, namely -6180 c, and is in satisfactory agreement with the value found when a solution containing 4 gram-molecules of hydrochloric acid react with 2 gram-molecules of sodium sulphate (*i.e.* -6730 c). We thus have additional evidence in support of the view that almost the whole of the hydrochloric acid may be regarded as existing in the free state. The process may also be *explained by the fact that hydrochloric acid, owing to its strong affinity for caustic soda, is able to decompose the sulphate*, so that sodium chloride is formed, and stannic hydroxide is thrown out of solution (see *Therm. Unters.*, i. 221).

Tin tetrachloride, $SnCl_4$, corresponds to a dibasic acid H_2SnCl_6, which however cannot exist in dilute aqueous solution, but, as already described, is changed to a solution of stannic hydroxide in hydrochloric acid.

The same thing happens with the soluble salts of this acid, as, for example, potassium stannichloride, K_2SnCl_6. This is shown by comparing the thermal values on solution in water of $SnCl_4$, $2KCl$, and K_2SnCl_6 with the heat of reaction of

stannic chloride upon potassium chloride in aqueous solution, namely—

$$\begin{matrix} x \\ -3376\text{ c} \end{matrix}\left|\begin{matrix}(SnCl_4,\ 2KCl)+\\ (K_2SnCl_6,\ Aq)\end{matrix}\right\}=\left\{\begin{matrix}(SnCl_4,\ Aq)+\\ (2KCl,\ Aq)+\\ (SnCl_4Aq,\ 2KClAq)\end{matrix}\right|\begin{matrix}+29{,}920\text{ c}\\ -\ 8{,}880\\ -\ \ 252\end{matrix}$$

from which it follows that—

$$x = (SnCl_4,\ 2KCl) = 24{,}164\text{ c.}$$

It thus appears that stannic and potassium chlorides, in the anhydrous state, unite together with a large evolution of heat, namely 24,164 c, whilst an aqueous solution of the same substances has a very small heat of reaction, namely −252 c (see also the tables in Chapter XI.).

G. Lead.

The heat of oxidation of lead is derived from the thermal effect on precipitation of the metal by means of zinc from a dilute solution of lead acetate made slightly acid with acetic acid. The concentration of the solution was $Pb(C_2H_3O_2)_2 + 400H_2O$; the thermal effect for 1 gram-atom of lead is 34,950 c, which is consequently the difference between the heats of formation of the acetates of zinc and lead.

It has already been shown that—

$$(Zn,\ O,\ H_2O) = 82{,}680\text{ c}$$
$$(ZnO_2H_2,\ 2C_2H_4O_2Aq) = 18{,}030,$$

and on addition we obtain the thermal effect on formation of zinc acetate in aqueous solution from zinc, oxygen, and acetic acid—

$$(Zn,\ O,\ 2C_2H_4O_2Aq) = 100{,}710\text{ c.}$$

Now, since the heat of formation of lead acetate under similar conditions is 34,950 c less than that of zinc acetate, we obtain for the former value—

$$(Pb,\ O,\ 2C_2H_4O_2Aq) = 65{,}760\text{ c,}$$

and if, finally, the heat of neutralization on formation of the salt

$$(PbO,\ 2C_2H_4O_2Aq) = 15{,}460\text{ c}$$

be subtracted, we have left the *heat of formation of anhydrous lead oxide*—

$$(Pb, O) = 50{,}300 \text{ c.}$$

I have deduced *the heats of formation of the chloride, bromide, and iodide of lead* from a series of experiments, in some of which the heats of solution of the substances named were measured, in others the heats of reaction on precipitation of aqueous solutions of lead nitrate by the addition of the respective potassium halides.

The three lead halides are known to be very sparingly soluble in water; but nevertheless, by the adoption of special methods, the determination of the heats of solution of the chloride and bromide was successfully performed, namely—

$$(PbCl_2, Aq) = -\ 6{,}796 \text{ c}$$
$$(PbBr_2, Aq) = -10{,}040.$$

Lead iodide, on the other hand, is too sparingly soluble for any such determinations.

In the other series of experiments I found the thermal effect on precipitation of a solution of lead nitrate by means of the potassium halide; which, after making the necessary correction for the slight solubility of the chloride and bromide of lead, amounted to—

$$(PbN_2O_6Aq, 2KClAq) = 4{,}460 \text{ c}$$
$$(PbN_2O_6Aq, 2KBrAq) = 8{,}020$$
$$(PbN_2O_6Aq, 2KIAq) = 13{,}790.$$

From these figures the heats of formation of the three halides can be found in the usual manner, namely—

Reaction	Q = Cl	Q = Br	Q = I
$(PbN_2O_6Aq, 2KQAq)$	4,460 c	8,020 c	13,790 c
(Pb, O, N_2O_5Aq)	68,070	68,070	68,070
$2(K, Q, Aq)$	202,340	180,460	150,040
Sum	274,870 c	256,550 c	231,900 c
(K_2, O, N_2O_5Aq)	192,100	192,100	192,100
(Pb, Q_2)	82,770 c	64,450 c	39,800 c

The formation of the same compounds by the action of lead oxide upon an aqueous solution of the halogen acids, gave the following thermal values :—

$$\left.\begin{array}{ll}(PbO, 2HClAq) & = 22{,}190 \text{ c} \\ (PbO, 2HBrAq) & = 25{,}750 \\ (PbO, 2HIAq) & = 31{,}520\end{array}\right\} \text{on complete precipitation.}$$

If now we add to these numbers the heats of solution of the chloride and bromide of lead, namely -6800 c and -10040 c respectively, it follows that—

$$\left.\begin{array}{ll}(PbO, 2HClAq) & = 15{,}390 \text{ c} \\ (PbO, 2HBrAq) & = 15{,}710\end{array}\right\} \text{without precipitation of the halides.}$$

The heat of solution of lead iodide, as already mentioned, was not measured.

The last figures show that the thermal values on solution of lead oxide in hydrochloric or hydrobromic acid are of equal magnitude; that is to say, lead oxide has the same heat of neutralization for hydrochloric as for hydrobromic acid, when the compounds formed remain in solution. Thus, here again, the behaviour is the same as in the case of the bases already described, with the single exception of cadmium.

For the heats of formation of the other compounds of lead, the tables in Chapter XI. must be consulted.

H. Thallium.

Thallium is, in many respects, an interesting metal. Its high density and small affinity for oxygen remind us most of lead and the noble metals; from the composition of its lower oxide (Tl_2O), the solubility of this latter in water, and the crystallographic properties of its salts, as well as from the spectrum of the metal, it approaches nearest to the alkali metals; the sparing solubility of the sulphur and halogen compounds, on the other hand, resembles that of the corresponding compounds of copper, mercury, and silver, whilst it is distinguished from these metals by the properties of its higher oxide.

The investigation comprises a large number of calorimetric

experiments, of which the most important results will now be given (see *Therm. Unters.*, vol. iii. pp. 338–354).

The determination of *the heats of solution of thallous oxide and thallous hydroxide* gave the following results:—

$$\left.\begin{aligned}(Tl_2O, Aq) &= -3080\\ 2(TlOH, Aq) &= -6310\end{aligned}\right\}\ \text{Heat of solution}$$
$$(Tl_2O, H_2O) = +3230 \quad \text{„ hydration.}$$

Thus both the oxide and hydroxide dissolve in water with absorption of heat, whilst the corresponding compounds of the alkali metals are dissolved with a very large evolution of heat. The affinity for water is but small, the heat of hydration of thallous oxide being only 3230 c, and the hydroxide is readily dehydrated by gentle warming, whilst the alkali hydroxides are not decomposed in this manner.

The heats of solution of thallous nitrate and thallous sulphate are also negative, namely—

$$(TlNO_3, Aq) = -9970 \text{ c}$$
$$(Tl_2SO_4, Aq) = -8280,$$

in which respect thallium is in complete agreement with the alkali metals. This resemblance is still further emphasized by a comparison of the differences between the heats of solution of the nitrates and sulphates, which are shown in the table below to be the same for the compounds of thallium and of the alkalies:—

	$R = Tl$	$R = K$	$R = Na$	$R = NH_4$
$(R_2N_2O_6, Aq)$	−19,940 c	−17,040 c	−10,060 c	−12,649 c
(R_2SO_4, Aq)	− 8,280	− 6,380	+ 460	− 2,370
Difference	−11,660 c	−10,660 c	−10,520 c	−10,270 c

Thallous chloride has likewise a negative heat of solution. And since the compound is very sparingly soluble in water, the determination of this value necessitated a very large number of experiments; the result was—

$$(TlCl, Aq) = -10,100 \text{ c.}$$

On the other hand, I was not able to measure the heats of solution of the corresponding bromide and iodide, owing to their still greater insolubility.

The heat of neutralization of thallous hydroxide by means of sulphuric and nitric acids is exactly equal to that of the alkalies, namely—

$$(2TlOHAq, H_2SO_4Aq) = 31{,}130 \text{ c}$$
$$(TlOHAq, HNO_3Aq) = 13{,}690.$$

On neutralization with hydrochloric acid the greater part of the thallous chloride is precipitated; but since the heat of solution of the latter is known from the preceding experiments, we can calculate, from the observed thermal effect, what the corresponding value would be for a complete precipitation of the chloride; we thus find

$(TlOHAq, HClAq) = 23{,}840$ c on complete precipitation.

If, now, we add to this number the heat of solution of thallous chloride ($-10{,}100$ c), we obtain the *absolute heat of neutralization of thallous hydroxide;* that is, the thermal effect when the thallous chloride remains in solution, namely—

$(TlOHAq, HClAq) = 13{,}740$ c when there is no precipitation.

This value is in complete agreement with the thermal effect on neutralization of the alkalies by means of hydrochloric acid (13,780 c), and it is therefore evident that the *heat of neutralization* of thallous hydroxide is in all three cases, namely, with respect to sulphuric, nitric, and hydrochloric acids, the *same as that of the alkalies*, provided that the reacting substances, as well as the products formed, all remain in solution.[1]

The heat of neutralization of *thallic hydroxide* was only measured in the case of hydrobromic acid, and the value found was

$$(Tl_2O_3H_3, 3HBrAq) = 30{,}680 \text{ c.}$$

The heat of formation of thallous oxide was determined by dissolving the metal in sulphuric acid of strength $SO_3 . 50H_2O$, when a solution of thallous sulphate is formed and hydrogen

[1] See footnote on p. 299.

is liberated. The heat evolution is very small, namely, 1060 c for 2 gram-atoms of metal.

From this value, on addition of the heat of formation of 1 gram-molecule of water, and after applying the necessary correction for the concentration of the acid, it is found that—

$$(Tl_2, O, SO_3Aq) = 70{,}290 \text{ c},$$

which, on subtraction of the heats of neutralization (31,130 c) and of solution (-3080 c) of thallous hydroxide, gives—

$$(Tl_2, O, Aq) = 39{,}160 \text{ c}$$
$$(Tl_2, O) = 42{,}240.$$

The heats of formation of the halides of thallium can now be determined in the usual manner, by measuring the thermal value of the action of the bromide and iodide of potassium upon thallous sulphate, when we find that—

$$(Tl, Cl) = 48{,}580 \text{ c}$$
$$(Tl, Br) = 41{,}290$$
$$(Tl, I) = 30{,}180.$$

Thallic bromide, $TlBr_3$, in aqueous solution, is readily reduced to the thallous condition by means of sulphur dioxide. From the thermal value of this process, in which sulphuric acid and thallous bromide are formed, we can calculate the heat of formation of thallic bromide in aqueous solution, namely—

$$(Tl, Br_3, Aq) = 56{,}450 \text{ c},$$

and from this we find in the usual manner—

$$(Tl, O_3, H_3) = 145{,}710 \text{ c}$$
$$(Tl_2, O_3, 3H_2O) = 86{,}340.$$

Thallic hydroxide is known to be precipitated as a dark-brown substance on direct oxidation of an aqueous solution of thallous hydroxide, this process being accompanied by a considerable evolution of heat, thus—

$$(Tl_2, O, Aq) + (Tl_2OAq, O_2) = (Tl_2, O_3, 3H_2O),$$
$$39{,}160 \text{ c} + 47{,}180 \text{ c} = 86{,}340 \text{ c},$$

so that the heat of oxidation is 47,180 c for each gram-molecule of oxygen taken up. This large evolution of heat

explains the readiness with which aqueous solutions of thallous hydroxide are oxidized on exposure to air. For other values, see the tables in Chapter XI.

J. Mercury.

1. In order to determine the thermal effect on combination of a metal with other substances, such as oxygen, chlorine, etc., we must, as already described, study some process in which the metal enters as such, either as the starting-point or else as the end-product. The calculation of the thermal effect on formation of compounds of zinc, aluminium, iron, etc., is based upon the values obtained on solution of the metal in acid; whilst in the case of copper and other metals the reverse process must be adopted, namely, the precipitation of the metal from its compounds by means of a metal of known thermal properties. Since mercury does not dissolve in very dilute acid, we must therefore choose some process for this metal in which mercury is separated in the metallic state.

When in the year 1874 I carried out some researches on mercury, I took as my starting-point the thermal effect of the well-known reaction of sulphurous acid upon a mercurous salt in aqueous solution, in which a black substance was precipitated, which at the time was taken for mercury. Fourteen years later (1888), however, *Nernst* showed that this precipitate was not pure mercury, and it was therefore necessary to introduce a correction for those values which were calculated from the thermal effect of this process. I was thus obliged to seek some other process as my starting-point, in which mercury is precipitated in a pure state. This is known to be the case when mercurous iodide, Hg_2I_2, is treated with a solution of potassium iodide; there is then formed a solution of potassium mercuric iodide, (K_2HgI_4), whilst half of the mercury is separated as metal. On the other hand, when mercurous iodide is treated with iodine in potassium iodide it dissolves completely with the formation of 2 molecules of potassium mercuric iodide for each molecule of the mercurous salt. The difference between the thermal values of these two processes corresponds,

therefore, to the formation of 1 molecule of potassium mercuric iodide in aqueous solution, and the difference as found experimentally amounted to 29,090 c per gram-molecule, so that—

$$(Hg, I_2, 2KIAq) = 29{,}090 \text{ c.}$$

2. For the further investigation it was necessary to have additional data at our disposal, the determination of which will now be described. Of the mercuric halides, only the chloride and cyanide are soluble in water; their *heats of solution* gave the following values:—

$$(HgCl_2, Aq) = -3300 \text{ c} \quad . \quad . \quad . \quad . \quad (a)$$
$$(HgC_2N_2, Aq) = -2970 \quad . \quad . \quad . \quad . \quad . \quad (b)$$

All three mercuric halides are, however, soluble respectively in solutions of the chloride, bromide, and iodide of potassium. The thermal values of these processes were measured directly, and the results were—

$$(HgCl_2, 2KClAq) = -\ 1{,}380 \text{ c} \quad . \quad . \quad . \quad (c)$$
$$(HgBr_2, 2KBrAq) = +\ 1{,}640 \quad . \quad . \quad . \quad (d)$$
$$(HgI_2, 2KIAq) = +\ 3{,}450 \quad . \quad . \quad . \quad (e)$$
$$(HgCl_2, 2KBrAq) = +\ 4{,}760 \quad . \quad . \quad . \quad (f)$$
$$(HgBr_2, 2KClAq) = -\ 4{,}340 \quad . \quad . \quad . \quad (g)$$
$$(HgCl_2, 2KIAq) = +23{,}450 \quad . \quad . \quad . \quad (h)$$

In the first five instances there is complete solution; in the last, however, mercuric iodide is precipitated, owing to which there is a considerable evolution of heat.

The following values, which have already been determined, are also available (see tables):—

$$2(K, Cl, Aq) = 202{,}340 \text{ c} \quad . \quad . \quad . \quad (i)$$
$$2(K, Br, Aq) = 180{,}460 \quad . \quad . \quad . \quad (k)$$
$$2(K, I, Aq) = 150{,}040 \quad . \quad . \quad . \quad (l)$$
$$(K_2, O, Aq) = 164{,}560 \quad . \quad . \quad . \quad (m)$$

3. As already found—

$$(Hg, I_2, 2KIAq) = 29{,}090 \text{ c,}$$

and since

$$(Hg, I_2) + (HgI_2, 2KIAq) = (Hg, I_2, 2KIAq),$$

it follows, by means of the value (*e*), that the heat of formation of *mercuric iodide* is

$$(Hg, I_2) = 25{,}640 \text{ c.}$$

From this, by making use of the values (*h*), (*i*), and (*l*), we can now calculate the *heat of formation of mercuric chloride;* for since

$$(h) = (Hg, I_2) + 2(K, Cl, Aq) - (Hg, Cl_2) - 2(K, I, Aq),$$

it follows that—

$$(Hg, Cl_2) = 54{,}490 \text{ c.}$$

4. The heat of formation of mercurous chloride, Hg_2Cl_2, was derived from the thermal effect of the action of chlorine upon mercurous chloride mixed with a solution of potassium chloride. The experimental results were as follows:—

$$(Hg_2\ Cl_2,\ Cl_2,\ 4KClAq) = 41{,}010 \text{ c.}$$

In this process, 2 gram-molecules of K_2HgCl_4Aq are formed.

The observed thermal value, $R = 41{,}010$ c, is composed of the following terms, of which the second corresponds to (*c*):—

$$R = 2(Hg, Cl_2) + 2(HgCl_2, 2KClAq) - (Hg_2, Cl_2)$$
$$41{,}010 \text{ c} = 108{,}980 \text{ c} - 2{,}760 \text{ c} - (Hg_2, Cl_2)$$

Whence it follows that the *heat of formation of mercurous chloride* is

$$(Hg_2, Cl_2) = 65{,}210 \text{ c.}$$

5. The difference between the heats of formation of mercurous chloride, bromide, and iodide was then estimated by means of the thermal effect on precipitation of mercurous nitrate, $(Hg_2N_2O_6)$, with an equivalent amount of aqueous solutions of the chloride, bromide, and iodide of potassium respectively. The heats of reaction were—

	$Q = Cl$	$Q = Br$	$Q = I$
$(Hg_2N_2O_6Aq, 2KQAq)$	24,320 c	31,940 c	42,510 c

In this process 2 gram-molecules of KNO_3 and 1 gram-

molecule of Hg_2Q_2 were formed. The observed thermal effect can be resolved into the following terms:—

$$(Hg_2N_2O_6Aq,\ 2KQAq) = \begin{cases} +(Hg_2,\ Q_2) + (K_2,\ O,\ N_2O_5Aq) \\ -2(K,\ Q,\ Aq) - (Hg_2,\ O,\ N_2O_5Aq) \end{cases}$$

and calculating by means of the numbers already quoted in (*i*), (*k*), and (*l*), we find—

	$Q = Cl$	$Q = Br$	$Q = I$
$(Hg_2N_2O_6Aq,\ 2KQAq)$	24,320 c	31,940 c	42,510 c
$2(K,\ Q,\ Aq)$	202,340	180,460	150,040
	226,660	212,400	192,550
$(K_2,\ O,\ N_2O_5Aq)$	192,100	192,100	192,100
$(Hg_2,\ Q_2) - (Hg_2,\ O,\ N_2O_5Aq)$	34,560 c	20,300 c	450 c

Now, since $(Hg_2,\ Cl_2)$ is equal to 65,210 c (see above), it follows that—

$$(Hg_2,\ O,\ N_2O_5Aq) = 65{,}210 \text{ c} - 34{,}560 \text{ c} = 30{,}650 \text{ c}$$
$$(Hg_2,\ Br_2) = 30{,}650 + 20{,}300 = 50{,}950$$
$$(Hg_2,\ I_2) = 30{,}650 + 450 = 31{,}100.$$

Moreover, since the heat of neutralization of mercurous nitrate, as previously described, is 5790 c, and

$$(Hg_2,\ O,\ N_2O_5Aq) = (Hg_2,\ O) + (Hg_2O,\ N_2O_5Aq),$$

the *heat of formation of mercurous oxide* is

$$(Hg_2O) = 24{,}860 \text{ c}.$$

6. From the preceding value for $(Hg_2,\ Br_2)$ we can now calculate the heat of formation of mercuric bromide in the same way as the heat of formation of mercurous chloride was derived from that of mercuric chloride, that is to say, by treating mercurous bromide with a solution of potassium bromide and bromine. The thermal value of this process was shown to be

$$(Hg_2Br_2,\ Br_2,\ 4KBrAq) = 36{,}080 \text{ c};$$

two molecules of K_2HgBr_4 being formed in solution. This

value, namely R, can, similarly to the above, be resolved into the following terms :—

$$R = 2(Hg, Br_2) + 2(HgBr_2, 2KBr) - (Hg_2, Br_2)$$
$$36{,}080 \text{ c} = 2(Hg, Br_2) + 3{,}280 \text{ c} - 50{,}950 \text{ c},$$

whence it follows that the *heat of formation of mercuric bromide* is

$$(Hg, Br_2) = 41{,}875 \text{ c}.$$

7. This last value can also be deduced from the thermal effect of the reciprocal processes quoted under (f) and (g); in the one case, mercuric chloride is dissolved in an aqueous solution of an equivalent amount of potassium bromide; in the other, mercuric bromide is dissolved in potassium chloride solution. In both cases the resulting liquid has the same composition, namely, that which would arise from the simultaneous reaction between the five substances, Hg, K_2, Cl_2, Br_2, and Aq. According to thermochemical principles (cf. page 9), we therefore have—

$$(Hg, K_2, Cl_2, Br_2, Aq) = (Hg, Cl_2) + (K_2, Br_2, Aq) + (HgCl_2, 2KBrAq)$$
$$= (Hg, Br_2) + (K_2, Cl_2, Aq) + (HgBr_2, 2KClAq)$$

that is to say, the thermal effect is of equal magnitude in the two cases. On subtraction we find that

$$(Hg, Cl_2) - (Hg, Br_2) + (K_2, Br_2, Aq) - (K_2, Cl_2, Aq) + (f) - (g) = 0,$$

whence we can calculate from the values already given—

$$(Hg, Br_2) = 41{,}710 \text{ c}.$$

This number agrees very well with that found above, namely 41,875 c, which testifies to the accuracy of the experiments.

8. The heat of neutralization can be determined in the usual manner; the values found were

$$(Hg_2O, 2HNO_3Aq) = 5{,}790 \text{ c}$$
$$(HgO, 2HNO_3Aq = 6{,}400$$
$$(HgO, 2HClAq) = 18{,}920.$$

The small heat of neutralization with nitric acid is in agreement with the instability of the nitrates and their decomposition

on great dilution. On the other hand, the neutralization of mercuric oxide by means of hydrochloric acid produces a large evolution of heat, and the resulting solution has a neutral reaction.

Coupled with this great difference in the heats of reaction with nitric and hydrochloric acids is the observation that a solution of mercuric nitrate is completely decomposed by an equivalent amount of sodium chloride (or other chlorides), so that after the reaction the liquid contains only mercuric chloride and sodium nitrate. Calorimetrically investigated, we find that on mixing the two liquids an amount of heat is evolved corresponding to the difference between 18,920 c and 6400 c, so that the decomposition is complete.

This property can be utilized in a *method of titrating the free acid* in a solution of mercuric nitrate, by adding sodium chloride to the solution and then titrating with caustic soda until neutralization is complete, when mercuric oxide begins to separate. The amount of alkali required corresponds to the free acid in the nitrate solution, $Hg(NO_3)_2 + xHNO_3$.

9. From the heat of neutralization of mercuric chloride we can now deduce the *heat of formation of mercuric oxide;* namely—

$$(HgO,\ 2HClAq) = \begin{cases} (Hg,\ Cl_2,\ Aq) + (H_2,\ O) \\ -(Hg,\ O) - 2(H,\ Cl,\ Aq). \end{cases}$$

Substituting the values already determined, we obtain—

$$(Hg,\ O) = 22{,}000 \text{ c.}$$

Thus the principal values resulting from the researches on the heats of formation of mercury compounds are as follows:—

$(Hg_2,\ O) = 24{,}860$ c	$(Hg_2,\ Cl_2) = 65{,}210$ c	$(Hg, Cl_2) = 54{,}490$ c
$(Hg,\ O) = 22{,}000$	$(Hg_2, Br_2) = 50{,}950$	$(Hg, Br_2) = 41{,}880$
	$(Hg_2,\ I_2) = 31{,}100$	$(Hg,\ I_2) = 25{,}640$

Taking *Nernst's* determination, $(Hg,\ Br_2) = 40{,}500$ c, as the basis of calculation, the thermal values will be about 1300 c lower for each gram-atom of *free* mercury which enters into the reaction.

K. Silver.

The determination of the heats of formation of silver compounds does not present any difficulty. An aqueous solution of silver nitrate is precipitated by means of very finely divided copper (formed by decomposition of cuprous oxide with dilute sulphuric acid). The heat evolved in the reaction is the difference between the heats of formation of the nitrates of copper and silver—

$$(Cu,\ O,\ N_2O_5Aq) - (Ag_2,\ O,\ N_2O_5Aq) = 35{,}630 \text{ c.}$$

Now, since the first term has already been found to be 52,410 c, we obtain—

$$(Ag_2,\ O,\ N_2O_5Aq) = 16{,}780 \text{ c.}$$

Furthermore, since the heat of neutralization of silver oxide amounts to 10,880 c (see page 120), we obtain the *heat of formation*—

$$(Ag_2,\ O) = 5900 \text{ c};$$

that is to say, a number which is lower than the heat of oxidation of any of the metals already described. This, again, coincides with the easy decomposition of silver oxide with rise of temperature.

The heats of formation of the halides are derived from the thermal effect on precipitation of silver nitrate by means of the chloride, bromide, and iodide of potassium in aqueous solution; the experiments gave—

	$Q = \text{Cl}$	$Q = \text{Br}$	$Q = \text{I}$
$(AgNO_3Aq,\ KQAq)$	15,870 c	20,130 c	26,440 c

From this we find in the usual manner that—

$$(Ag,\ Cl) = 29{,}380 \text{ c}$$
$$(Ag,\ Br) = 22{,}700$$
$$(Ag,\ I) = 13{,}800.$$

The heats of neutralization of the oxide by means of nitric and sulphuric acids, and the heats of solution of the nitrate and sulphate were found—

$(AgNO_3,\ Aq) = -5440$ c $(Ag_2O,\ N_2O_5Aq) = 10{,}880$ c
$(Ag_2SO_4,\ Aq) = -4480$ $(Ag_2O,\ SO_3Aq) = 14{,}490.$

For the remaining values, see the tables in Chapter XI.

L. Gold.

Before I could, with advantage, undertake thermochemical measurements of the formation of compounds of gold, it was necessary to carry out a large number of experiments with the object of discovering trustworthy methods for the preparation of its most important compounds, more especially for the halides, and I eventually succeeded in preparing the following substances in an easy and reliable manner :—

$AuCl . AuCl_3$	$AuBr . AuBr_3$	AuCl
$AuCl_3$	$AuBr_3$	AuBr
$AuCl_3 . 2H_2O$	—	—
$HAuCl_4 . 4H_2O$	$HAuBr_4 . 5H_2O$	$Au(OH)_3$

The experiments are described in detail in *Therm. Unters.*, vol. iii. pp. 382–392, and also in the *Journ. f. praktische Chemie*, (2) vol. xiii. pp. 337 *et seq.* Here I shall give only a summary of the results.

1. Formation and Properties of the Compounds of Gold.

(*a*) *Aurous aurichloride*, $AuCl . AuCl_3$.—A solution of hydrogen aurichloride was precipitated by means of sulphurous acid; the precipitate was then boiled with dilute nitric acid, washed, and carefully dried at 170°, until the spongy gold was completely freed from adherent water. In this condition gold is readily attacked by dry chlorine, the reaction being accompanied by a large evolution of heat. It is not advisable to work with less than about 100 grams of gold, which latter is placed in a short U-tube and exposed to a rapid stream of dry chlorine. As soon as the air is displaced, the process is started by gently warming for a short time the place where the stream of chlorine first comes in contact with the gold. Directly the reaction begins the source of heat is removed, and the absorption of chlorine becomes very rapid and complete, and lasts until 12 litres of chlorine have been absorbed for every 100 grams of gold, after which the absorption suddenly

ceases. *Artificial heating must be carefully avoided*, since the product is thereby decomposed. In this manner 100 grams of gold can easily be converted into the compound $AuCl . AuCl_3$ within the space of half an hour. That the composition is in agreement with the formula has been confirmed by analysis.

Aurous aurichloride is a dark brown, hard substance, which can be easily triturated to a fine powder. It is very hygroscopic, and is decomposed by water into neutral auric and aurous chlorides, and these latter, on further action of water, are converted into auric chloride and metallic gold.

(*b*) *Anhydrous auric chloride*, $AuCl_3$, is easily prepared in the following manner: About 100 grams of aurous aurichloride are treated with just sufficient water to form a thick liquid, which then contains auric chloride. The decomposition takes place with a large evolution of heat, by means of which a part of the aurous chloride is converted into auric chloride and metallic gold. In each case the final decomposition can be accelerated by gently warming the liquid. When the gold has settled, the liquid is poured into a porcelain basin and cautiously evaporated, care being taken that the bottom only and not the sides of the vessel are exposed to the source of heat. The temperature is kept just below the boiling-point of the liquid. Evaporation then proceeds rapidly, and after a short time crystals are formed on the surface of the liquid. The evaporation is continued almost to dryness, with constant stirring, after which the final dehydration is completed in a drying-oven at about 150°. The product is anhydrous auric chloride, which is a dark brown substance, very hygroscopic, readily soluble in water with evolution of heat, and forming a dark brown solution even when very dilute.

(*c*) *Crystalline, hydrated auric chloride.*—If the evaporation of the above-mentioned auric chloride is stopped as soon as crystals begin to form upon the surface, the solution, on cooling in dry air, gives rise to large, dark, orange-coloured crystals, which are deliquescent in damp air, and have the composition $AuCl_3 + 2H_2O$. This compound gives up the whole of its water on standing for a few days over sulphuric acid.

(*d*) *Aurous chloride*, AuCl, is very readily formed on warming anhydrous auric chloride up to 185° in an open vessel placed in a drying-oven. In this manner about 100 grams of auric chloride can easily be converted into aurous chloride within the space of two hours.

(*e*) *Aurous auribromide*, $AuBr . AuBr_3$. — When finely divided gold, prepared by reduction with sulphurous acid and subsequent drying at 170°, is placed in a vessel and covered with bromine, a vigorous reaction ensues. After the excess of bromine has been evaporated off there remains an almost black, friable mass, which can be easily reduced to a state of fine powder. This is once more treated with bromine, and, after evaporating off the excess, the product is found to have the composition Au_2Br_4.

This compound, unlike the corresponding chloride, is not deliquescent; it is decomposed at 115°, leaving an impure aurous bromide. It is also slowly decomposed by water, and quickly by ether, with the production of $AuBr_3$, which dissolves, whilst the residue is mainly AuBr.

(*f*) *Anhydrous auric bromide*, $AuBr_3$.—A concentrated ethereal solution of $AuBr_3$ is decomposed on warming; but the liquid can be evaporated at ordinary temperatures by means of a strong current of air without decomposition of the bromide, since the temperature of the liquid is reduced to −20° (for further details see *Therm. Unters.*, iii. p. 387). The precipitated bromide is freed from traces of moisture by warming to 70°.

The anhydrous bromide, $AuBr_3$, is a very dark brown, crystalline powder, which does not deliquesce in the air; it dissolves slowly in water, but quickly in ether, and the solutions are of a very dark brown colour.

An aqueous solution is completely decolorized on addition of a very dilute solution of sulphurous acid, and then when potassium iodide is added a gold-coloured, powdery precipitate of auric iodide is formed.

By means of a stronger solution of sulphurous acid the bromide is completely reduced to metallic gold; this is precipitated in the form of a very fine powder, which retains

its pulverulent form even after drying, and is a *peculiar allotropic modification of gold* (see below).

(*g*) *Hydrogen auribromide*, $HAuBr_4 . 5H_2O$, *deserves special mention amongst the compounds of gold*, since it is very easily formed, is stable in the air, and very readily crystallizes.

The compound can be easily prepared in the following manner: Pulverulent gold is treated with bromine, when aurous auribromide is formed. When the reaction is finished, the product is treated with 100 grams of a hydrobromic acid solution of 1·38 specific gravity for every 100 grams of gold, after which bromine is added until the gold is dissolved. The solution, which becomes much heated by the vigorous reaction, is poured into a basin and left to cool, when large, flat, needle-shaped crystals, often 3–4 centimetres long, are quickly formed. After about an hour nearly the whole of the liquid is converted into crystals. The mother-liquor is poured off, and the crystals are dried in air at a temperature not exceeding 20°. Recrystallization can be brought about by adding a small percentage of water to the crystals and warming to 30°, when they melt in their water of crystallization; on cooling, the substance crystallizes out afresh. The compound is of a dark brown colour, and is stable in the air at low temperatures; *at 27° it melts in its water of crystallization;* at lower temperatures it does not lose weight in the air, nor on standing over lime or sulphuric acid.

(*h*) *Aurous bromide*, AuBr.—When hydrogen auribromide is warmed slightly above its melting-point (27°) it loses water and hydrobromic acid, and is converted into a solid mass. This latter is then warmed in a drying-oven to 115°, and repeatedly broken up and pulverized. Bromine and hydrobromic acid are again given off, the colour of the substance becomes gradually lighter, and finally yellowish-grey, and the powder so formed looks very much like talc. When the weight becomes constant, the analysis shows the composition to be AuBr.

Aurous bromide is a greyish-yellow, talc-like substance, stable in air, and readily converted into a fine powder. It is insoluble as such in water, but is thereby decomposed on careful heating into auric bromide and metallic gold.

(*i*) *Auric hydroxide*, $Au(OH)_3$, is easily prepared in the following manner: A very dilute solution of neutral auric chloride, containing 1 molecule of $AuCl_3$ in about 800 molecules of H_2O, is mixed with an exactly equivalent quantity of caustic soda solution and warmed. The solution is at first light yellow, later dark brown. A solution of sodium sulphate is then added, when auric hydroxide is precipitated of a dark brown colour, not unlike ferric hydroxide. The mother-liquor is decanted off, and the precipitate washed upon the filter until the filtrate no longer contains either sulphuric or hydrochloric acid. The powder is rinsed off the filter, covered with strong nitric acid, and warmed, after which it is again decanted and washed.

Auric hydroxide is a dark brown, very heavy powder, which is insoluble in water, but dissolves easily in dilute hydrobromic acid, and more slowly in hydrochloric acid.

(*k*) *Hydrogen aurichloride*, $HAuCl_4 . 4H_2O$. — The finely pulverized and dry substance crystallizes with 4 molecules of water. The earlier statement by *Weber*, that it contained only 3 molecules of water, applied to a partially dehydrated substance; this was proved by the determination of the heats of solution given below (see p. 296) for the compound with 3 and with 4 molecules of water.

2. Thermal Effect on Formation of Compounds of Gold.

(*a*) The thermal effect on formation of all the compounds of gold mentioned above has been measured. The research was very protracted, since over twenty reactions had to be studied. No small difficulty was encountered from the fact that gold was found to be precipitated from its solutions in no less than *three well-characterized allotropic forms*, depending upon the character of the compound and of the precipitant. With reference to the numerous experimental details connected with this research I must refer the reader to *Therm. Unters.*, vol. iii. pp. 392–413; here I shall give only a summary of the results.

(*b*) *The heat of reaction on solution of auric hydroxide in*

hydrochloric and in hydrobromic acids was measured directly; the result was

$$\left.\begin{array}{l}(AuO_3H_3, 4HClAq) = 22{,}970 \text{ c} \\ (AuO_3H_3, 4HBrAq) = 36{,}780\end{array}\right\} \text{Difference } 13{,}810 \text{ c.}$$

In these cases, therefore, there are formed solutions containing $HAuCl_4$ and $HAuBr_4$.

The thermal values of the reaction between solutions of neutral auric chloride and hydrochloric acid, and of that between neutral auric bromide and hydrobromic acid were likewise measured directly, with the following results:—

$$(AuCl_3Aq, HClAq) = 4530 \text{ c}$$
$$(AuBr_3Aq, HBrAq) = 7700.$$

On subtracting these numbers from those above, we obtain

$$\left.\begin{array}{l}(AuO_3H_3, 3HClAq) = 18{,}440 \text{ c} \\ (AuO_3H_3, 3HBrAq) = 29{,}080\end{array}\right\} \text{Difference } 10{,}640 \text{ c.}$$

Thus in these reactions neutral solutions of the halides $AuCl_3$ and $AuBr_3$ are formed.

It is noteworthy that *in these reactions hydrobromic acid produces a greater thermal effect than hydrochloric acid.* To verify this behaviour control experiments were made, in which the difference in thermal effect was also measured indirectly, namely, by the thermal value of the reaction between equivalent solutions of auric chloride and hydrobromic acid, and also between that of auric bromide and hydrochloric acid. The result was

$$\left.\begin{array}{l}(AuCl_3Aq, 3HBrAq) = 15{,}209 \text{ c} \\ (AuBr_3Aq, 3HClAq) = 4279\end{array}\right\} \text{Difference } 10{,}930 \text{ c}$$
$$\left.\begin{array}{l}(HAuCl_4Aq, 4HBrAq) = 13{,}805 \text{ c} \\ (HAuBr_4Aq, 4HClAq) = -509\end{array}\right\} \text{ " } 14{,}314.$$

According to the law relating to the thermal effect of reciprocal processes (see pp. 9 and 113), the difference between the thermal values of the two connected reciprocal processes must in this case be equal to the difference between the direct measurements already described of the heats of reaction of the halogen acids with auric hydroxide, namely, 10,640 c and

13,810 c respectively. This satisfactory agreement testifies to the probable accuracy of the values found. Moreover, the last two experiments show that $HAuCl_4Aq$ in aqueous solution is almost completely decomposed to $HAuBr_4$ by an equivalent amount of hydrobromic acid ($4HBr$).

(*c*) *The heats of formation of auric chloride, auric bromide, and auric hydroxide* can be derived from the thermal effect on precipitation of an auric chloride solution by means of aqueous sulphurous acid. The experimental results for neutral auric chloride were

$$(AuCl_3Aq, \tfrac{3}{2}SO_2Aq) = 83{,}600 \text{ c.}$$

From this number the heat of formation of auric hydroxide can be derived in the following manner :—

$$\left.\begin{matrix} x \\ 2\times 18{,}440 \text{ c} \\ 2\times 83{,}600 \end{matrix}\right| \left.\begin{matrix} (Au_2,\ O_3,\ 3H_2O) + \\ 2(Au\,O_3H_3, 3HClAq) + \\ 2(AuCl_3Aq,\ \tfrac{3}{2}SO_2Aq) \end{matrix}\right\} = 3(SO_2Aq, O) \Big| 3\times 63630 \text{ c}$$

The gold in the three processes on the left side of the equation is converted into the metallic state, whilst the sulphurous acid is oxidized to sulphuric acid. According to the calculation—

$$x = (Au_2,\ O_3,\ 3H_2O) = -13{,}190 \text{ c.}$$

The heat of formation of auric hydroxide is therefore negative, which is in accordance with the ease with which it is decomposed. Gold is the only one amongst the metals investigated which has a negative heat of oxidation; silver, which comes next to gold, has a heat of oxidation of +5900 c.

From the heat of formation of auric hydroxide we can, in the usual manner, calculate that of auric chloride and of the bromide, since the result of the three reactions on the left side is equal to $3(H_2, O)$ and $2(Au,\ Cl_3,\ Aq)$; namely—

$$\left.\begin{matrix} -13{,}190 \text{ c} \\ +6\times 39320 \text{ c} \\ +2\times 18440 \end{matrix}\right| \left.\begin{matrix} (Au_2,\ O_3,\ 3H_2O) + \\ 6(H,\ Cl,\ Aq) + \\ (Au_2O_3{\cdot}3H_2O, 6HClAq) \end{matrix}\right\} = \left\{\begin{matrix} 3(H_2,\ O) \\ 2(Au, Cl_3, Aq) \end{matrix}\right| \begin{matrix} 3\times 68360 \text{ c} \\ 2\,x \end{matrix}$$

Hence it follows that the heat of formation of *auric chloride* is

$$(Au, Cl_3, Aq) = 27{,}265 \text{ c}$$
$$(Au, Cl_3, HClAq) = 31{,}795.$$

By substituting bromine for chlorine in the preceding equation, and making use of the corresponding values—

$(H, Br, Aq) = 28{,}380$ c or $(Au_2O_3 . 3H_2O, 6HBrAq) = 58{,}160$ c,

we obtain the heat of formation of *auric bromide* in aqueous solution—

$$(Au, Br_3, Aq) = 5{,}085 \text{ c}$$
$$(Au, Br_3, HBrAq) = 12{,}785.$$

(*d*) *Allotropic forms of gold.*—On precipitation of a solution of *auric chloride with sulphurous acid* the metal is separated as a spongy, coarse, yellow powder, which contracts very much on drying. This is the usual form in which gold separates.

On the other hand, the precipitation of *auric bromide with aqueous sulphurous acid* throws down the gold as a finely divided dark powder, without metallic appearance, which does not change its form on stirring or standing, or even on drying; on stronger heating it first contracts into large lumps, and is then converted into the first-mentioned modification.

Finally, when *aurous bromide or iodide is reduced by means of aqueous sulphurous acid*, or decomposed by the aid of aqueous hydrochloric or hydrobromic acid, the gold is separated as a very fine yellow powder with metallic lustre, which even after drying retains its metallic powdery appearance.

My researches thus prove the existence of three *distinct allotropic modifications* of gold; that is to say, forms which contain different amounts of energy, and consequently give different thermal values when converted into the same compound. I shall represent these three modifications of the gold atom as Au, Au_α, and Au_β. Moreover, the *difference in the amount of energy* of a gram-atom of gold in the three allotropic forms is

$$(Au_\alpha) = (Au) + 3475 \text{ c}$$
$$(Au_\beta) = (Au) + 4667 \text{ c}.$$

These differences are found in the following manner :—

In modification Au_α the gold is precipitated from an auric bromide solution by means of sulphurous acid; the experimental thermal value was as follows :—

$$(HAuBr_4Aq,\ 2SO_2Aq) = 61{,}785 \text{ c.}$$

From this number we can calculate the heat of formation of $(Au,\ Br_3,\ Aq)$ in a similar manner to that used above, when $AuCl_3Aq$ was reduced by means of SO_2Aq. We thus have—

$$\left.\begin{array}{r|l} x & (Au_\alpha,\ Br_3,\ Aq) + \\ 77{,}00 \text{ c} & (AuBr_3Aq,\ HBrAq) + \\ \frac{3}{2} \times 68{,}360 & \frac{3}{2}(H_2,\ O) + \\ 61{,}785 & (HAuBr_4Aq, \frac{3}{2}SO_2Aq) \end{array}\right\} = \left\{\begin{array}{l|l} 3(H, Br, Aq) + & 3 \times 28{,}380 \text{ c} \\ \frac{3}{2}(SO_2\ Aq,\ O) & \frac{3}{2} \times 63{,}630. \end{array}\right.$$

whence it follows that—

$$(Au_\alpha,\ Br_3,\ Aq) = 8560 \text{ c},$$

whilst we found above—

$$(Au,\ Br_3,\ Aq) = 5085 \text{ c.}$$

The difference between these two numbers is equal to the *difference between the amount of energy associated with the gram-atom of gold in the two modifications*, thus—

$$(Au_\alpha) = (Au) + 3475 \text{ c.}$$

The following investigations will give us some information as to the energy relations of the third modification (Au_β).

(*e*) *Aurous chloride, aurous bromide, and aurous iodide.*— When a solution of neutral auric chloride reacts with an equivalent solution of potassium iodide, we have—

$$AuCl_3 + 3KI = AuI + 3KCl + I_2;$$

the experimental thermal value is

$$(AuCl_3Aq,\ 3KIAq) = 45{,}660 \text{ c.}$$

This result is made up of the following terms :—

$$(Au, I) + 3(K, Cl, Aq) - (Au, Cl_3, Aq) - 3(K, I, Aq) = 45{,}660 \text{ c}$$
$$(Au, I) + 3 \times 101{,}170 \text{ c} - 27{,}265 \text{ c} - 3 \times 75{,}020 \text{ c} = 45{,}660,$$

and the heat of formation of *aurous iodide* will be

$$(Au, I) = -5525 \text{ c.}$$

When *aurous iodide is reduced by means of aqueous sulphurous acid*, the gold is separated in *the third modification* as a fine powder with metallic lustre; the thermal value is

$$(2AuI, SO_2Aq) = 23{,}397 \text{ c},$$

and contains the following terms:—

$$(SO_2Aq, O) + 2(H, I, Aq) - 2(Au_\beta, I) - (H_2, O) = 23{,}397 \text{ c}$$
$$63{,}530 \text{ c} + 2 \times 13{,}170 \text{ c} - 2(Au_\beta, I) - 68{,}360 \text{ c} = 23{,}397,$$

whence it follows that—

$$(Au_\beta, I) = -893 \text{ c},$$

whilst it was found above that—

$$(Au, I) = -5525 \text{ c}.$$

The difference between these two values gives

$$(Au_\beta) - (Au) = 4632 \text{ c}.$$

This value can also be determined in another way, so that we are able to check the accuracy of the former measurement. By the *reduction of aurous bromide with aqueous sulphurous acid*, and similarly also on decomposition of aurous bromide and aurous chloride by means of the corresponding halogen acid, the gold is also separated as the modification Au_β. The experimental thermal values for the processes described were as follows:—

$$(2AuBr, SO_2Aq) = 42{,}760 \text{ c}$$
$$(3AuBr, HBrAq) = 3{,}652$$
$$(3AuCl, HClAq) = 4{,}976.$$

In the *first* case the reaction is

$$2AuBr + H_2O + SO_2Aq = 2Au_\beta + 2HBrAq + SO_3Aq.$$

If now we put the difference

$$(Au_\beta) - (Au) = x,$$

then the total thermal effect will be composed of the following terms:—

$$42{,}760 \text{ c} = (SO_2Aq, O) + 2(H, Br, Aq) - (H_2, O) - 2(Au, Br) - 2x$$
$$= 63{,}630 \text{ c} + 2 \times 28{,}380 \text{ c} - 68{,}360 \text{ c} - 2(AuBr) - 2x.$$

From which we find that—

$$(Au, Br) = 4635 - x.$$

In the *second* case, namely, the decomposition of aurous bromide by means of hydrobromic acid, the process is

$$3AuBr + HBrAq = HAuBr_4Aq + 2Au_\beta$$

and the corresponding thermal effect—

$$3652 = (Au, Br_3, HBrAq) - 3(Au, Br) - 2x.$$

In the *third* example the formula is the same, only that *Cl* must be substituted for *Br*. We then have—

$$(Au, Br) = 3044 - \tfrac{2}{3}x$$
$$(Au, Cl) = 8940 - \tfrac{2}{3}x.$$

By comparing the two estimations of (Au, Br), we obtain

$$(Au, Br) = 4635 - x = 3044 - \tfrac{2}{3}x,$$

whence it follows that—

$$x = 4773 \text{ c};$$

whilst researches on the iodide gave a value of 4632 c, which is therefore in very satisfactory agreement. Thus the mean value taken from

$$\tfrac{1}{3}x = 1591 \text{ c and } x = 4632 \text{ c}$$

is 4667 c, and we consequently have—

$$x = (Au_\beta) - (Au) = 4667 \text{ c}.$$

Substituting these values for x in the heats of formation found above for *AuCl* and *AuBr*, we obtain, in round numbers—

$$(Au, Cl) = \quad 5830 \text{ c}$$
$$(Au, Br) = - \quad 70$$
$$(Au, I) = - 5520,$$

that is to say, the heat of formation corresponds to that of the common modification of gold.

(*f*) *The heats of solution of the compounds of gold soluble in water* are as follows :—

Substance.	Heat of solution.
$AuCl_3$	+ 4,450 c
$AuBr_3$	− 3,760
$AuCl_3 . 2H_2O$	− 1,690
$HAuCl_4 . 4H_2O$	− 5,830
$HAuCl_4 . 3H_2O$	− 3,550
$HAuBr_4 . 5H_2O$	− 11,400

By the aid of these numbers we find that—

$$(Au, Cl_3) = 22{,}815 \text{ c}$$
$$(Au, Br_3) = 8{,}845.$$

A comparison of the heat of solution of $HAuCl_4$ with 4 and with 3 gram-molecules of water shows that the last-mentioned salt is partially dehydrated, and the difference exactly corresponds to the difference in the heats of solution previously found (see pp. 63 *et seq.*) for 1 gram-molecule of water in partially dehydrated salts. The heat of solution of $AuCl_3$ is positive (+4450 c), for $AuBr_3$, on the other hand, it is negative (−3760 c); we may therefore conclude, and this is confirmed by experiment, that $AuCl_3$ is able to combine with water (see p. 58), but that $AuBr_3$, on the contrary, is unable to do so. The compound $AuCl_3 . 2H_2O$ has a negative heat of solution (−1690 c) similarly to the other hydrated compounds.

M. Platinum.

1. Modes of Formation of the Compounds of Platinum Investigated.

It is of the utmost importance that the platinum compounds required for thermochemical research should be prepared in large quantities and in a pure state. This object was achieved in the following manner :—

(*a*) *Potassium platinochloride*, K_2PtCl_4, which was formerly

prepared by very tedious methods, is *readily obtained by the reaction between cuprous chloride and potassium platinichloride in aqueous solution.* Potassium platinichloride is mixed with water, so that it forms a thick, pulpy mass, and the mixture is then warmed, but not, however, allowed to boil. Next, precipitated and moist cuprous chloride is gradually added until a small quantity only of the platinic salt remains undecomposed. The two sparingly soluble salts are mutually decomposed to form two soluble salts, namely, potassium platinochloride and cupric chloride, of which the former is, for the most part, precipitated on cooling, and can be easily purified by recrystallization. If a little water only is employed in the process, we can, in the first crystallization, recover from 70 to 80 per cent. of the platinochloride formed in a very nearly pure condition. The salt, owing to the ease with which it is formed and to its great crystallizing power, which allows of rapid purification, is of special value as the starting-point for the formation of other compounds of platinum (see *Therm. Unters.*, iii. p. 413).

(*b*) *Hydrogen platinochloride*, H_2PtCl_4, is easily prepared on precipitation of a warm, concentrated solution of potassium platinochloride by means of hydrogen platinichloride, H_2PtCl_6. On cooling, the potassium platinichloride formed is precipitated; a small portion only remaining dissolved in the red, concentrated solution of hydrogen platinochloride. From this solution double salts can be directly prepared by the addition of metallic chlorides and subsequent crystallization.

(*c*) *Ammonium platinochloride* is in this manner readily formed by adding an equivalent amount of ammonium chloride to the hydrogen platinochloride; on concentration and cooling, the salt crystallizes out in large red needles.

(*d*) *Platinous hydroxide.*—A dilute solution of potassium platinochloride (1 gram-molecule to 300 gram-molecules of water) is carefully mixed with an equal volume of an equivalent solution of dilute caustic soda. When the resulting liquid is heated to boiling, the whole of the platinum is precipitated as the lower hydroxide, whilst the solution, which was originally strongly alkaline, is now quite neutral.

The lower hydroxide is a black powder, which easily dissolves in dilute hydrochloric or hydrobromic acid on gentle warming. *Formic acid, even in very dilute solution, reduces it to the metal with evolution of carbon dioxide.*

(*e*) *Potassium platinobromide*, K_2PtBr_4, is an easily soluble salt, which, on slow crystallization of the solution, forms large, nearly black crystals, apparently rhombic octahedra; on rapid crystallization, needles of a red-brown colour are formed. The salt is prepared by boiling the concentrated solution of a mixture of 1 gram-molecule of K_2PtCl_4 and 4 gram-molecules of NaBr. The greater part of the sodium chloride formed crystallizes out immediately on cooling; the remainder is separated by repeated recrystallization.

(*f*) *Sodium platinibromide*, $Na_2PtBr_6 + 6H_2O$, is formed when a concentrated solution of hydrogen platinichloride (H_2PtCl_6) is mixed with 6 gram-molecules of hydrobromic acid; on evaporating to dryness, hydrogen chloride is given off. A little water and 2 gram-molecules of NaBr are next added, the solution is then evaporated to dryness, the residue dissolved, and the salt recrystallized.

2. Thermal Effect on Formation of Compounds of Platinum.

(*a*) *Hydrogen platinichloride*, H_2PtCl_6, is a dibasic halogen acid, 1 gram-molecule of which in solution exactly neutralizes 2 gram-molecules of sodium hydroxide. Investigations have proved that the evolution of heat is not altered by adding an excess of soda; the numerical results were

a	(*H_2PtCl_6Aq, a NaOHAq*)
2	27,216 c
4	27,240
6	27,336.

The heat of neutralization is thus exactly equal in magnitude to that of 2 gram-molecules of the other strong halogen acids, hydrochloric, hydrobromic, and hydriodic, namely, 27,300 c as against 27,400 c. Hence it follows that—

When a molecule of anhydrous platinic chloride, $PtCl_4$ combines with two equivalents of an aqueous solution of the chloride of a metal (either of the alkalies, alkaline earths, or magnesium group of metals) *to form a double chloride soluble in water, the thermal effect is always the same, and corresponds to the action of platinic chloride upon an equivalent amount of hydrochloric acid in aqueous solution.*

We may therefore assume that the double chloride can be formed in two ways: in the *first*, when platinic chloride is dissolved in hydrochloric acid, and the solution formed is subsequently neutralized with the respective base; in the *second*, the base is first neutralized with hydrochloric acid, and the platinic chloride is then dissolved in this liquid.

In both cases the same final products are obtained from the same constituents, and the total thermal effect will therefore be the same in the two cases;[1] we have, for example—

$$\left.\begin{matrix}(PtCl_4,\ 2HClAq) \\ +\ H_2PtCl_6Aq,\ 2NaOHAq)\end{matrix}\right\} = \left\{\begin{matrix}2(NaOHAq,\ HClAq) \\ +(PtCl_4,\ 2NaClAq).\end{matrix}\right.$$

Now, since the heats of neutralization are equal for equivalent amounts of H_2PtCl_6Aq and $HClAq$, it follows that—

$$(PtCl_4,\ 2HClAq) = PtCl_4,\ 2NaClAq), \text{ etc.};$$

that is to say, 1 gram-molecule of $PtCl_4$ gives the same thermal effect with an equivalent amount of a solution of hydrochloric acid or of the chloride mentioned, which is of importance in calculating the heats of formation of the double chlorides.

(*b*) *The heats of solution* of the more important compounds of platinum have been measured directly with the following results:—

Salt.	Heat of solution.	Salt.	Heat of solution.
K_2PtCl_6	−13,760 c	K_2PtBr_6	−12,260 c
Na_2PtCl_6	+ 8,540	Na_2PtBr_6	+ 9,900
$Na_2PtCl_6 . 6H_2O$	−10,630	$Na_2PtBr_6 . 6H_2O$	− 8,550
K_2PtCl_4	−12,220	K_2PtBr_4	−10,630
$(NH_4)_2PCl_4$	− 8,480		

[1] *Note by Translator.*—In each case the heat evolved is that due to the union of 2H with 2OH, according to generally accepted theories.

Here, again, we observe that, as with the majority of salts, the heats of solution are *negative* for the saturated, hydrated salts, and also for the salts which have no water of crystallization; on the other hand, they are *positive* for the anhydrous compounds, Na_2PtCl_6 and Na_2PtBr_6, corresponding to the hydrated salts (see p. 59).

(*c*) *The heats of formation of the chlorine and bromine compounds of platinum* are derived from the thermal effect on reduction of the latter in aqueous solution by means of metallic cobalt, in which reaction metallic platinum and cobaltous chloride or bromide are formed. For example—

$$(Na_2PtCl_6Aq : Co) = 2(Co, Cl_2, Aq) - (Pt, Cl_4, 2NaClAq) = R.$$

It follows from the facts already mentioned that—

$$(Co, Cl_2, Aq) = 94{,}820 \text{ c} = A$$
$$(Co, Br_2, Aq) = 72{,}940 \text{ c} = B,$$

so that the heats of formation of the platinum salts are found as the difference between $2A$ (and respectively A, B, or $2B$) and R. The following are the experimental values for R:—

$$R_1 = 2A - (Pt, Cl_4, 2NaClAq)^1 = 105{,}020 \text{ c}$$
$$R_2 = A - (Pt, Cl_2, 2KClAq) = 52{,}990$$
$$R_3 = 2B - (Pt, Br_4, 2KBrAq) = 88{,}720$$
$$R_4 = B - (Pt, Br_2, 2KBrAq) = 41{,}010.$$

If now we substitute the values of A and B in the four equations, we obtain

$$\left.\begin{aligned}(Pt, Cl_4, 2NaClAq) &= 84{,}620 \text{ c}\\ (Pt, Cl_2, 2KClAq) &= 41{,}830\end{aligned}\right\} \text{Difference, } 42{,}790 \text{ c}$$

$$\left.\begin{aligned}(Pt, Br_4, 2KBrAq) &= 57{,}160\\ (Pt, Br_2, 2KBrAq) &= 31{,}930\end{aligned}\right\} \text{Difference, } 25{,}230 \text{ c.}$$

Note by Translator.—NaCl is used here in place of KCl, because otherwise the sparingly soluble K_2PtCl_6 would be precipitated, whilst the other reactions studied all give rise to soluble potassium salts. This substitution is admissible since the heats of neutralization of the alkalies are of equal value, and it has been shown on p. 299 that ($PtCl_4$, 2NaClAq) = ($PtCl_4$, 2KClAq).

According to the statement made under (*a*) the thermal effect is the same whether the platinum salt contains K_2, Na_2, Mg, etc. These values were controlled in the following manner :—

(*d*) The given difference between two connected numbers is equal to the difference between the heats of formation of the corresponding compounds; thus for example—

$$42{,}790\text{c} = (Pt, Cl_4, 2KClAq) - (Pt, Cl_2, 2KClAq) = (K_2PtCl_4Aq, Cl_2).$$

When, therefore, a solution of K_2PtCl_4 is converted into K_2PtCl_6 by means of chlorine the thermal effect must be equal to 42,790 c. This was proved by special experiments. In one series of these a solution of Na_2PtCl_6 was reduced to Na_2PtCl_4 by the addition of Cu_2Cl_2; the thermal effect of the process was 16,640 c, and this corresponds to

$$16{,}640\text{ c} = (Cu_2Cl_2,\ Cl_2,\ Aq) - (Na_2PtCl_4Aq,\ Cl_2).$$

Now, since (Cu_2Cl_2, Cl_2, Aq) is equal to 59,670 c, we obtain 43,030 c for (Na_2PtCl_4Aq, Cl_2), which is the required thermal effect of the reaction.

In a second series of experiments a solution of potassium platinobromide was mixed with bromine; the heat of reaction was 25,350 c, which corresponds to the reaction (K_2PtBr_4Aq, Br_2). These values confirm those found above by direct experiment; namely—

$$(K_2PtCl_4Aq,\ Cl_2) = \begin{cases} 42{,}790\text{ c} & \text{determined by subtraction } (c) \\ 43{,}030 & \text{,,} \quad \text{directly} \end{cases}$$

$$(K_2PtBr_4Aq,\ Br_2) = \begin{cases} 25{,}230 & \text{,,} \quad \text{by subtraction } (c) \\ 25{,}350 & \text{,,} \quad \text{directly.} \end{cases}$$

The agreement is thus very satisfactory.

(*e*) *The affinity of platinum for oxygen* is measured by the reduction of platinous hydroxide by means of formic acid (see p. 298). The reaction proceeds very readily, with the formation of carbon dioxide, water, and metallic platinum. The thermal effect amounts to 44,800 c, and corresponds to the reaction

$$(CH_2O_2,\ O) - (Pt,\ O,\ H_2O) = 44{,}800\text{ c.}$$

Now, since my later researches have shown that the heat of oxidation of liquid formic acid is 64,020 c (see *Therm. Unters.*,

iv. 181), it follows that the *heat of formation of platinous hydroxide* is

$$(Pt, O, H_2O) = 19{,}220 \text{ c.}$$

The affinity of platinum for oxygen is thus very considerable; the heat of formation of the lower oxide lies between the heats of formation of silver and mercuric oxides.

(*f*) From the values given above we can calculate the thermal effect of a number of reactions in which platinum takes part. For example—

$$2(H, Cl, Aq)+(Pt, O, 4HClAq) = (Pt, Cl_2, 2HClAq)+(H_2, O)$$
$$4(H, ClAq)+(Pt, O_2, 6HClAq) = (Pt, Cl_4, 2HClAq)+2(H_2, O)$$

whence it follows that—

$(Pt, O, 4HClAq) = 31{,}550$ c | $(Pt, O, 4HBrAq) = 43{,}440$ c
$(Pt, O_2, 6HClAq) = 64{,}060$ | $(Pt, O_2, 6HBrAq) = 80{,}360$.

The heats of reaction are very considerable, and, as the figures show, *the value is very much greater for hydrobromic than for hydrochloric acid*; a precisely similar relation has already been noted in the case of auric oxide (see p. 290).

From the known thermal values the heats of formation of the compounds of platinum in the solid state can now be calculated in the usual manner. The numbers will be found in the subsequent tables.

N. Palladium.

Palladium approximates very closely in properties to platinum; but a marked difference is, however, observed in the case of the hydroxides. Dilute solutions of the double chlorides of palladium are decomposed at ordinary temperatures by dilute solutions of caustic soda, with the precipitation of either $PdO . H_2O$ or $PdO_2 . 2H_2O$; whilst $PtO . H_2O$, as already described, is precipitated only after boiling, and the higher hydroxide neither at ordinary temperatures nor on boiling.

(*a*) *Chlorides of potassium and palladium.*—Thermochemical researches have been carried out on the two salts K_2PdCl_4 and K_2PdCl_6. The heat of formation of each of these salts has

been determined in two ways. For example, K_2PdCl_4 was reduced in aqueous solution, *either* by means of metallic cobalt, *or else* of cuprous chloride; in both cases metallic palladium was precipitated, and the thermal effect was—

$$(K_2PdCl_4Aq : Co) = 47{,}330 \text{ c}$$
$$(K_2PdCl_4Aq : Cu_2Cl_2) = 11{,}320.$$

From which, by means of the values already determined, we find—

$$(Pd, Cl_2, 2KClAq) \left\{ \begin{matrix} 47{,}490 \text{ c} \\ 48{,}350 \end{matrix} \right\} \text{ Mean value, } 47{,}920 \text{ c.}$$

The heat of formation of potassium palladochloride in the solid state can be derived in the usual manner from the values just given; namely—

$$\left. \begin{matrix} (Pd, Cl_2, 2KCl) \\ + (K_2PdCl_4, Aq) \end{matrix} \right\} = \left\{ \begin{matrix} 2(K, Cl, Aq) \\ + (Pd, Cl_2, 2KClAq). \end{matrix} \right.$$

Now, since the heats of solution of K_2PdCl_4 and of 2KCl are respectively $-13{,}630$ c and -2×4440 c, we obtain

$$(Pd, Cl_2, 2KCl) = 52{,}670 \text{ c};$$

that is to say, when crystallized potassium palladochloride is formed in the reaction between metallic palladium, chlorine, and crystallized potassium chloride, the thermal effect is 52,670 c.

(*b*) *Palladous iodide.*—From the heat of formation of potassium palladochloride, and from the thermal effect of its decomposition by means of potassium iodide in aqueous solution, we obtain the heat of formation of *palladous iodide.* The experimental result was

$$(K_2PdCl_4Aq, 2KIAq) = 22{,}560 \text{ c},$$

whence we find in the usual manner—

$$(Pd, I_2, H_2O) = 18{,}180 \text{ c}.$$

(*c*) *Potassium palladichloride.*—The heat of formation of this salt was also measured in two ways—*both* by the reaction between the crystallized salt, cuprous chloride, and water, when metallic palladium is precipitated, *and also* by the

action of the crystallized salt upon a solution of potassium iodide, when palladous iodide and iodine are separated. In these experiments I was obliged to make use of crystallized K_2PdCl_6, instead of its solution, since the salt is partially decomposed by water. The result was—

$$(K_2PdCl_6,\ 2Cu_2Cl_2,\ Aq) = 31{,}610 \text{ c} = R.$$

The thermal value, R, is composed of the following terms :—

$$R = -(Pd,\ Cl_4,\ 2KCl) + 2(KCl,\ Aq + 2(Cu_2Cl_2,\ Cl_2,\ Aq),$$

and by means of the values already determined we find that—

$$(Pd,\ Cl_4,\ 2KCl) = 78{,}850 \text{ c}.$$

The other series of experiments gave the following result :—

$$(K_2PdCl_6,\ 4KIAq) = 34{,}620 \text{ c} = R_1,$$

and the heat of reaction was composed of the following terms :—

$$R_1 = \begin{cases} -(Pd,\ Cl_4,\ 2KCl) + 2(KCl,\ Aq) + 4(K,\ Cl, Aq) \\ -4(K,\ I,\ Aq) \qquad + (Pd,\ I_2,\ H_2O). \end{cases}$$

Since, according to p. 303, the heat of formation of palladous iodide is equal to 18,180 c, we find that $R_1 = 79{,}280$ c.

Thus as the result of the two determinations—

$$(Pd,\ Cl_4,\ 2KCl) = \left\{ \begin{matrix} 78{,}850 \text{ c} \\ 79{,}280 \end{matrix} \right\} \text{ Mean value, } 79{,}060 \text{ c}.$$

(*d*) *Palladous hydroxide and palladic hydroxide.*—The corresponding double chlorides, Na_2PdCl_4 and K_2PdCl_6, were decomposed by means of dilute caustic soda solution; the former was used in aqueous solution, the latter as the crystalline salt (see (*c*)). The result was

$$(Na_2PdCl_4Aq,\ 2NaOHAq) = 12{,}550 \text{ c}$$
$$(K_2PdCl_6,\ 4NaOHAq) \quad = 18{,}010.$$

From these numbers we find in the usual manner—

$$(Pd,\ O,\ H_2O) = 22{,}710 \text{ c}$$
$$(Pd,\ O_2,\ 2H_2O) = 30{,}430$$

as the heats of formation of palladous and palladic hydroxides.

If the value 12,550 c found above is subtracted from the heat

of neutralization of 2 gram-molecules of sodium hydroxide, that is to say, from 27,490 c we obtain the thermal effect on solution of palladous hydroxide in hydrochloric acid, namely—

$$(PdO_2H_2,\ 4HClAq) = 14{,}940 \text{ c.}$$

In a similar manner from the other value, namely 18,010 c, we can find the heat of solution of palladic hydroxide in hydrochloric acid—

$$(PdO_4H_4,\ 6HClAq) = 21{,}970 \text{ c.}$$

There is, however, some uncertainty about this number, since, owing to its partial decomposition by water, the heat of solution of K_2PdCl_6 cannot be accurately measured.

(*e*) *Hydrogen palladochloride in aqueous solution behaves as a dibasic acid;* its heat of neutralization with respect to sodium hydroxide is

$$(H_2PdCl_4Aq,\ 2NaOHAq) = 27{,}250 \text{ c,}$$

which is thus equal to the heat of neutralization of hydrogen platinichloride by an equivalent amount of the monobasic halogen acids. Hence it follows that as in the case of platinic chloride—

$$(Pd,\ Cl_2,\ 2HClAq) = (Pd,\ Cl_2,\ 2KClAq), \text{ etc.}$$

The last reaction was found above to equal 47,920 c, therefore—

$$(Pd,\ Cl_2,\ 2HClAq) = 47{,}920 \text{ c.}$$

See also the following tables.

O. Carbonates of the Metals.

For the calculation of the heats of formation of the salts of carbonic acid we require, in addition to the thermal values already given, a knowledge of the heats of neutralization of the different carbonates. The heat of neutralization of sodium hydroxide by means of carbonic acid has already been

given (see p. 98); that of the other bases can be deduced from the thermal effect on double decomposition of the soluble salts with equivalent solutions of sodium carbonate. The concentration used was $Na_2CO_3 + 400H_2O$, $BaCl_2 + 400H_2O$, etc.; and the metals investigated were barium, strontium, calcium, manganese, cadmium, lead, and silver, *all of which form anhydrous carbonates.*

The following characteristics were noted: Barium carbonate is precipitated, immediately and completely, in a stable amorphous state, and the thermal effect at once attains its maximum value. *Strontium* carbonate is also precipitated in the amorphous condition; but after an interval of two or three minutes it becomes crystalline, and this change is accompanied by a slightly *increased* thermal effect. *Calcium* carbonate behaves in the same way, but the formation of crystals is attended by a small *absorption of heat.* The carbonates of cadmium, manganese, lead, and silver form amorphous precipitates, which also show a further slight evolution of heat after the initial reaction; but the salts do not become crystalline.

The experimental results were as follows: The thermal effect on decomposition of an aqueous solution of 1 gram-molecule of sodium carbonate by means of an equivalent amount of—

$BaCl_2$	amounts to	+ 1,350 c
$SrCl_2$	,,	230
$CaCl_2$	,,	− 2,080
$MnSO_4$	,,	− 2,050
$CdSO_4$	,,	+ 370
$Pb(NO_3)_2$	,,	+ 6,110
$2AgNO_3$	,,	+ 10,480.

According to the researches already described—

$$\left.\begin{array}{l}(Na_2OAq,\ CO_2) = 26{,}060 \text{ c} \\ (Na_2OAq,\ CO_2Aq) = 20{,}180\end{array}\right\} (CO_2,\ Aq) = 5880 \text{ c},$$

and we can therefore, in the usual manner, derive the following

values from the known thermal effects of the reactions taking place by double decomposition :—

Reaction in solution.		Reaction with dry substance.	
B	(B, CO_2Aq)	RO	(RO, CO_2)
Na_2OAq	20,180 c	—	—
$BaOAq$	21,820	BaO	62,220 c
$SrOAq$	20,550	SrO	55,770
$CaOAq$	18,310	CaO	42,520
$Mn(OH)_2$	13,230	—	—
$Cd(OH)_2$	13,370	—	—
PbO	16,700	PbO	22,580
Ag_2O	14,180	Ag_2O	20,060

The reactions in the first column take place between aqueous solutions of carbonic acid and of either the hydroxide or the anhydride of the base specified; but in the other column the reaction was between gaseous carbon dioxide and the anhydrous oxides. From these last values we can again calculate the heats of formation of the anhydrous carbonates from their elements (see tables).

The value found for the formation of calcium carbonate is of practical importance in "lime-burning,"

$$(CaO, CO_2) = 42{,}520 \text{ c},$$

since it gives the amount of heat required to decompose the carbonate into lime and carbon dioxide.

P. Sulphides of the Metals.

It has previously been stated (see p. 103) that hydrogen sulphide in aqueous solution behaves as a monobasic acid towards the soluble bases (alkali metals and alkaline earths) and also towards magnesium hydroxide. The molecule in aqueous solution must therefore correspond to the formula H.SH, and, like the halogen acids (hydrochloric, hydrobromic, and hydriodic), hydrogen sulphide shows an equal heat of neutralization for all these bases, but this value is, however,

10,030 c lower than in the case of the halogen acids. The compounds formed are hydrosulphides of the formulæ RSH and $R(SH)_2$. These are all soluble in water, even $Mg(SH)_2$, which is easily prepared by the decomposition of $MgSO_4$ and $Ba(SH)_2$ in aqueous solution.

Hydrogen sulphide behaves quite differently towards the oxides of the heavy metals; since these, when acted upon by this acid, form insoluble sulphides, some of which are hydrated, others anhydrous, as, for example, the sulphides of lead and mercury.

The thermochemical investigation of these compounds was carried out in the following manner: A solution of a metallic salt was precipitated by means of an equivalent solution of sodium sulphide, Na_2S, or, better still, a mixture of NaSH and NaOH. The degree of dilution of all the liquids was 400 gram-molecules of water, thus $Na_2S+400H_2O$, $MnSO_4 . 400H_2O$, etc. The experimental results were as follows:—

Q	(QAq, Na_2SAq)	Q	(QAq, Na_2SAq)
$MnSO_4$	7,790 c	$CuSO_4$	36,440 c
$FeSO_4$	13,220	Cu_2Cl_2	43,540
$NiSO_4$	15,090	$HgCl_2$	46,050
$CoSO_4$	16,310	$Pb(NO_3)_2$	30,980
$ZnSO_4$	18,130	$2TlNO_3$	33,740
$CdSO_4$	27,120	$2AgNO_3$	67,180

By means of these figures, we can now easily calculate *the heat of formation of the sulphides* of the metals. If we put

$$(QAq,\ Na_2SAq) = R$$

and represent the metallic constituent of Q by M, we have for the seven reactions, in which the sulphates are acted upon by sodium sulphide—

$$R=(M,\ S)+(Na_2,\ O,\ SO_3Aq)-(M,\ O,\ SO_3Aq)-(Na_2,\ S,\ Aq).$$

Now, according to the preceding researches (see tables)—

$$(Na_2,\ O,\ SO_3Aq) = 186{,}640 \text{ c}$$
$$(Na_2,\ S,\ Aq) = 101{,}990,$$

and therefore—

$$(M, S) = R + (M, O, SO_3Aq) - 84{,}650 \text{ c.}$$

In the same way, for the reactions in which the chlorides of copper and mercury are acted upon by sodium sulphide—

$$(M, S) = R + (M, Cl_2, Aq) - 91{,}030 \text{ c,}$$

and for the reactions with the nitrates of lead, thallium, and silver—

$$(M, S) = R + (M, O, N_2O_5Aq) - 80{,}630 \text{ c.}$$

The following table contains the thermal values, calculated in this manner, of the direct formation of the sulphides of the metals from *rhombic* (octahedral) *sulphur* and the metal in question :—[1]

M	R	(M, O, SO_3Aq)	(M, S)
Mn	7,790 c	121,250 c	44,390 c
Fe	13,220	93,200	21,770
Ni	15,090	86,950	17,390
Co	16,310	88,070	19,730
Zn	18,130	106,090	39,570
Cd	27,120	89,880	32,350
Cu	36,440	55,960	7,750[2]
		(M, Cl_2, Aq)	
Cu_2	43,540	65,750	18,260
Hg	46,050	51,190	6,210
		(M, O, N_2O_5Aq)	
Pb	30,980	68,070	18,420
Tl_2	33,740	66,540	19,650
Ag_2	67,180	16,780	3,330

[1] The differences between the values given for (M, S) in the fourth column of this table, and those found in *Therm. Unters.*, iii. 455, are due to the fact that the last-mentioned numbers were calculated for amorphous sulphur (see p. 195).

[2] On precipitation of a copper sulphate solution with sulphuretted hydrogen, or sodium sulphide, it is not CuS which is formed, but a compound with a smaller amount of sulphur, namely Cu_4S_3, and free sulphur (see *Therm. Unters.*, iii. p. 449), and a comparison of the heat of formation of this substance with that found for Cu_2S, shows that the affinity of copper for sulphur is in all essentials satisfied with the formation of the last-mentioned sulphide.

The behaviour of hydrogen sulphide with solutions of salts.—For purpose of comparison, we make use of the thermal effect of the reaction of sulphuretted hydrogen water upon the nitrates, all of which are soluble in water. The thermal value can in this case be divided between the following terms :—

$$(RN_2O_6Aq,\ H_2SAq) = \begin{cases} (R,\ S) - (R,\ O,\ N_2O_5Aq) \\ +(H_2,\ O) - (H_2,\ S,\ Aq). \end{cases}$$

All the terms on the right-hand side of the equation are known; on the other, we find by difference—

$$68{,}360\ \text{c} - 7{,}290\ \text{c} = 61{,}070\ \text{c}.$$

The thermal values of the other reactions are given below for some of the metals—

R	$(R,\ S,\ nH_2O)$	$(R,\ O,\ N_2O_5Aq)$	$(RN_2O_6Aq,\ H_2SAq)$
Mn	44,390 c	117,720 c	−12,260 c
Fe	21,770	89,620	− 6,780
Ni	17,390	83,420	− 4,960
Co	19,730	84,540	− 3,740
Zn	39,570	102,510	− 1,860
Cd	32,350	86,300	+ 7,120
Pb	18,420	68,070	+11,420
Tl_2	19,650	66,540	+14,180, etc.

The thermal effect of the reaction between the nitrates and hydrogen sulphide in aqueous solution, resulting in the precipitation of a metallic sulphide, is therefore *negative* for Mn, Fe, Ni, Co, and Zn; it is, on the other hand, *positive* for Cd, Pb, Tl, Cu, Hg, and Ag. This is in complete agreement with the properties of these metals so serviceable in analysis. The metals of the last-mentioned group are precipitated by sulphuretted hydrogen with evolution of heat; but this is not the case with those first mentioned. *Zinc* forms the connecting link; in neutral solutions of the zinc salts of the strong acids sulphuretted hydrogen produces a slight precipitation, which ceases as soon as the liquid becomes sufficiently acid. On the other hand, with acetic, lactic, or other weak acids, of which the heat of neutralization is less than that of nitric acid, there is complete

precipitation. The heat of neutralization of acetic acid is about 2000 c lower than that of nitric acid, and the thermal effect on precipitation of a solution of a zinc salt containing acetic acid is therefore approximately equal to zero.

Q. Cyanides of the Metals.

My researches on the heats of formation of cyanogen compounds were restricted to the cyanides of K, Ag, Hg, Cd, and Zn. A large number of the cyanides of the metals are insoluble in water, but they are readily dissolved by aqueous solutions of potassium cyanide. This is the case with silver, mercury, and in part with zinc, since zinc cyanide is not quite insoluble. On the other hand, cadmium cyanide dissolves in water, but all the same it reacts vigorously with potassium cyanide in aqueous solution. The thermochemical measurements led to the following results :—

(*a*) *Potassium cyanide.*—All the values necessary for calculating the heat of formation of this compound have already been given, namely—

$(K, O, H, Aq) = 116{,}460$ c $(H, CN, Aq) = 11{,}470$ c
$(KOHAq, HCNAq) = 2{,}770$ $(H_2, O) = 68{,}360$

and since the reaction is

$$KOHAq + HCNAq = KCNAq + H_2O$$

we obtain—

$$(K, CN, Aq) = 116{,}460 + 11{,}470 + 2{,}770 - 68{,}360 \text{ c} = 62{,}340 \text{ c}.$$

Furthermore, the heat of solution of KCN is equal to − 3010 c, and we therefore have—

$$(K, CN) + (KCN, Aq) = (K, CN, Aq)$$
$$(K, CN) - 3010 = 62{,}340 \text{ c};$$

from which it follows that the thermal effect on formation of *anhydrous potassium cyanide* is

$$(K, CN) = 65{,}350 \text{ c},$$

when the reacting substances are metallic potassium and gaseous cyanogen. The heats of formation of the cyanides of

the other metals can now be derived from the thermal values of the reaction between potassium cyanide and the salts of the metals in question.

(*b*) *Silver cyanide.*—When an aqueous solution containing 1 gram-molecule of $AgNO_3$ is mixed with a solution of potassium cyanide which contains 2 gram-molecules of KCN, the soluble compound $KAg(CN)_2$ is formed. If the solution thus obtained is then mixed with a solution of 1 gram-molecule of $AgNO_3$, the whole of the silver is precipitated as cyanide. The thermal values of these two reactions are

$$(AgNO_3Aq,\ 2KCNAq) = 33{,}205 \text{ c}$$
$$(KAgC_2N_2Aq,\ AgNO_3Aq) = 20{,}221.$$

We may suppose these processes to be resolved into the following terms :—

$$33{,}205 \text{ c} = (AgNO_3Aq,\ KCNAq) + (AgCN,\ KCNAq)$$
$$20{,}221 \ \ = (AgNO_3Aq,\ KCNAq) - (AgCN,\ KCNAq),$$

and we then have for the sum and difference of these numbers—

$$53{,}426 \text{ c} = 2(AgNO_3Aq,\ KCNAq) = 2 \times 26{,}713 \text{ c}$$
$$12{,}984 \ \ = 2(AgCN,\ KCNAq) \ \ \ = 2 \times \ 6{,}492.$$

The thermal effect in the former case corresponds to the precipitation of silver cyanide from the nitrate solution and potassium cyanide ; in the latter, to a solution of silver cyanide in a solution of potassium cyanide. Now, since the heats of formation of silver nitrate and of potassium cyanide are known, it follows in the usual manner that—

$$(Ag_2,\ C_2N_2) = \ \ 2{,}786 \text{ c}$$
$$(Ag_2O,\ 2HCNAq) = 42{,}306.$$

The heat of formation of silver cyanide is thus very small, namely 2786 c, and the substance is also very easily decomposed on warming ; but the reaction between silver oxide and aqueous hydrocyanic acid is, on the other hand, accompanied by a very large evolution of heat, namely 42,306 c. The thermal effect on solution of 1 gram-molecule of AgCN in potassium cyanide is, as stated above, positive, namely 6492 c, and this shows that there is a very active reaction between the two substances.

(*c*) *Mercuric cyanide.*—The researches on the formation of mercuric cyanide were carried out in precisely the same manner as in the case of silver cyanide. The experiments show that—

$$(HgCl_2Aq, 4KCNAq) = 45{,}579 \text{ c}$$
$$(K_2HgC_4N_4Aq, HgCl_2Aq = 21{,}990.$$

From the sum and difference of these numbers it follows, as was the case for silver, that

$$(HgCl_2Aq, 2KCNAq) = 33{,}784 \text{ c}$$
$$(HgC_2N_2Aq, 2KCNAq) = 11{,}795;$$

and from this, in the same manner as above, we derive—

$$(Hg, C_2N_2, Aq) = 7{,}314 \text{ c}$$
$$(HgO, 2HCNAq) = 30{,}734.$$

Moreover, since the heat of solution of $Hg(CN)_2$ is -2965 c, we have—

$$(Hg, C_2N_2) = 10{,}279 \text{ c}$$

as the heat of formation of the crystalline mercuric cyanide. This value is very much greater than that found for silver cyanide; but otherwise the numbers are of about the same magnitude in the two cases.

(*d*) *Cadmium cyanide.*—The investigations were carried out on the same lines as the foregoing. The experiments show that—

$$(CdSO_4Aq, 4KCNAq) = 26{,}043 \text{ c}$$
$$(K_2CdC_4N_4Aq, CdSO_4Aq) = 4{,}459,$$

from which it follows, as above, that—

$$(CdSO_4Aq, 2KCNAq) = 15{,}251 \text{ c}$$
$$(CdC_2N_2Aq, 2KCNAq) = 10{,}792.$$

The last value is of special interest; for cadmium cyanide is soluble in water, and in solution reacts upon a solution of potassium cyanide without any change in the state of aggregation taking place, and yet the reaction is attended by an evolution of 10,792 c. This fact reminds us of the evolution of heat in the reactions between solutions of mercuric chloride

and mercuric bromide and of the chloride and bromide of potassium respectively.

From these values we can calculate in the same manner as above—

$$\left.\begin{array}{ll}(Cd,\ C_2N_2,\ Aq) & = 33{,}960 \\ (CdO_2H_2,\ 2HCNAq) & = 13{,}700 \\ (CdC_2N_2Aq,\ 2KCNAq) & = 10{,}790\end{array}\right\} 24{,}490 \text{ c.}$$

(*c*) *Zinc cyanide.*—The experiments were carried out in a similar manner to the preceding. The results were

$$\begin{array}{ll}(ZnSO_4\ Aq,\ 4KCNAq) & = 27{,}310 \text{ c} \\ (K_2ZnC_4N_4Aq,\ ZnSO_4Aq) & = 9{,}642 + y\end{array}$$

Since zinc cyanide is not altogether insoluble in water, the thermal effect of the last experiment must be rather lower than it would have been for complete precipitation; this small difference is represented below by *y*.

From these values we calculate as before—

$$\left.\begin{array}{ll}(ZnSO_4Aq,\ 2KCNAq) & = 18{,}476 + y \\ (ZnC_2N_2.aH_2O,\ 2KCNAq) & = 8{,}834 - y \\ (ZnO_2H_2,\ 2HCNAq) & = 16{,}140 + y \\ (Zn,\ C_2N_2,\ aH_2O) & = 53{,}400 + y\end{array}\right\} 24{,}974 \text{ c,}$$

It is worthy of note that the thermal effect on conversion of $Zn(OH)_2$ into $K_2Zn(CN)_4Aq$ is 24,974 c, and this is approximately equal to the corresponding thermal value when $Cd(OH)_2$ is converted into $K_2Cd(CN)_4Aq$, namely 24,490 c. On the other hand, the evolution of heat which is observed on dissolving the cyanides of the metals in a solution of potassium cyanide, when the double cyanides are formed, is not the same in the two cases, but is greatest for cadmium and least for zinc.

(*f*) *Formation of cyanogen.*—The usual method of preparing cyanogen in the free state is by heating mercuric cyanide. This decomposition, however, takes place only at a high temperature, when a greater part of the cyanogen is converted into paracyanogen. *Cyanogen is far more easily obtained by gently warming a mixture of equivalent quantities of*

mercuric cyanide and mercuric chloride, when mercurous chloride and cyanogen are formed—

$$Hg(CN)_2 + HgCl_2 = Hg_2Cl_2 + (CN)_2.$$

If the two substances, in a dry and finely divided state, are carefully mixed, the action takes place at a very low temperature, since the mixture melts with the evolution of cyanogen. The reason that mercuric cyanide is more easily decomposed in the presence of the chloride is certainly due to the fact that whilst the decomposition of the cyanide itself is attended by a heat-absorption of 10,280 c, the joint reaction takes place with an evolution of heat. The thermal value of the process is as follows:—

$$(Hg_2, Cl_2) - (Hg, C_2N_2) - (Hg, Cl_2) = R$$
$$65{,}210\text{ c} - 10{,}280\text{ c} - 54{,}590\text{ c} = 440\text{ c},$$

and it would naturally be still greater if it were not that the cyanogen produced is in the gaseous form.

It is noteworthy that even at the very low temperature at which this process takes place an appreciable amount of paracyanogen is formed; but this formation increases the heat of reaction.

CHAPTER XI

SYSTEMATIC REVIEW OF THE NUMERICAL RESULTS OF THE RESEARCHES ON COMPOUNDS OF THE METALS: OXIDES, HYDROXIDES, HALOGEN COMPOUNDS, SALTS, SULPHIDES, CYANIDES, ETC.

In order to render the numerical results of my researches on the thermal phenomena of the metals more easily available, I have arranged them in a series of tables, each table having reference to some particular compound. The following twenty-three metals were selected for study, namely—

Potassium.	Magnesium.	Cobalt.	Silver.
Sodium.	Aluminium.	Nickel.	Gold.
Lithium.	Manganese.	Copper.	Tin.
Barium.	Zinc.	Lead.	Palladium.
Strontium.	Cadmium.	Mercury.	Platinum.
Calcium.	Iron.	Thallium.	

The atomic weights used were those given in Table 1, pp. 48–52. In addition to the results for these metals, the tables also contain certain data referring to the metalloids—

Tellurium, Arsenic, Antimony, Bismuth,

the remaining thermal properties of which are fully described in the chapter on the non-metals, see Table 18. The atomic weights of these elements will be found on p. 45.

All the values given hold good at a temperature of about 18° C. and for the substances in their normal state of aggregation at that temperature, that is, for bromine, water, and mercury, as liquids, etc. In calculating the thermal effect of the calcium compounds, *Moissan's* value of (Ca, O) equals 145,000 c was used. In the case of barium compounds, x represents the unknown magnitude (Ba, O, H_2O).

TABLE 19.

CHLORIDES.

Reaction.	Heat of formation of the compound.	Heat of solution of the compound.	Heat of formation in aqueous solution.
(K_2, Cl_2)	211,220 c	− 8,880 c	202,340 c
(Na_2, Cl_2)	195,380	− 2,360	163,020
(Li_2, Cl_2)	187,620	+ 16,880	204,500
(Ba, Cl_2)	x + 48,240 [1]	+ 2,070	x +50,310 [1]
$(Ba, Cl_2, 2H_2O)$	x + 55,240 [1]	− 4,930	
(Sr, Cl_2)	184,560	+ 11,140	195,690
$(Sr, Cl_2, 6H_2O)$	203,190	− 7,500	
(Ca, Cl_2)	183,890	+ 17,410	201,300
$(Ca, Cl_2, 6H_2O)$	205,640	− 4,340	
(Mg, Cl_2)	151,010	+ 35,920	186,930
$(Mg, Cl_2, 6H_2O)$	183,980	+ 2,950	
(Al_2, Cl_6)	321,960	+153,690	475,650
(Mn, Cl_2)	111,990	+ 16,010	128,000
$(Mn, Cl_2, 4H_2O)$	126,460	+ 1,540	
(Zn, Cl_2)	97,210	+ 15,630	112,840
(Cd, Cl_2)	93,240	+ 3,010	96,250
$(Cd, Cl_2, 2H_2O)$	98,530	− 2,280	
(Fe, Cl_2)	82,050	+ 17,900	99,950
$(Fe, Cl_2, 4H_2O)$	97,200	+ 2,750	
(Fe_2, Cl_6)	192,080	+ 63,360	255,440
(Co, Cl_2)	76,480	+ 18,340	94,820
$(Co, Cl_2, 6H_2O)$	97,670	− 2,850	
(Ni, Cl_2)	74,530	+ 19,170	97,300
$(Ni, Cl_2, 6H_2O)$	94,860	− 1,160	
(Cu_2, Cl_2)	65,750	—	—
(Cu, Cl_2)	51,630	+ 11,080	62,710
$(Cu, Cl_2, 2H_2O)$	58,500	+ 4,210	
(Pb, Cl_2)	82,770	− 6,800	75,970
(Hg_2, Cl_2)	65,210	—	—
(Hg, Cl_2)	54,490	− 3,300	51,190
$(Hg, Cl_2, 2KCl, H_2O)$	60,620	− 16,390	44,230
(Tl_2, Cl_2)	97,160	− 20,200	76,900
(Ag_2, Cl_2)	58,760	—	—
(Au_2, Cl_2)	11,620	—	—
(Au, Cl_3)	22,820	+ 4,450	27,270
$(Au, Cl_3, 2H_2O)$	28,960	− 1,690	
$(Au, Cl_4, H, 4H_2O)$	76,950	− 5,830	71,120
(Sn, Cl_2)	80,790	+ 350	81,140
$(Sn, Cl_2, 2H_2O)$	86,560	− 5,370	
$(Sn, Cl_2, 2KCl, H_2O)$	85,680	− 13,420	72,260
(Sn, Cl_4) *liquid*	127,250	+ 29,920	157,170
$(Sn, Cl_4, 2KCl)$	151,400	− 3,380	148,020
$(Pd, Cl_2, 2KCl)$	52,670	− 13,630	39,040
$(Pd, Cl_4, 2KCl)$	79,060	− 15,000	64,060
$(Pt, Cl_2, 2KCl)$	45,170	− 12,220	32,950

Reaction.	Heat of formation of the compound.	Heat of solution of the compound.	Heat of formation in aqueous solution.
$(Pt, Cl_2, 2NH_4Cl)$	42,550	− 8,480	34,070
$(Pt, Cl_4, 2KCl)$	89,500	− 13,760	75,740
$(Pt, Cl_4, 2NaCl)$	73,720	+ 8,540	82,260
$(Pt, Cl_4, 2NaCl, 6H_2O)$	92,890	− 10,630	
(Te, Cl_4)	77,380	+ 20,340	97,720
(As, Cl_3) *liquid*	71,390	+ 17,580	88,970
(Sb, Cl_3)	91,390	(see p. 229)	—
(Sb, Cl_5) *liquid*	104,870		—
(Bi, Cl_3)	90,630		—

TABLE 20.

BROMIDES.

Reaction.	Heat of formation of the compound.	Heat of solution of the compound.	Heat of formation in aqueous solution.
(K_2, Br_2)	190,620 c	− 10,160 c	180,460 c
(Na_2, Br_2)	171,540	− 380	171,160
$(Na_2, Br_2, 4H_2O)$	180,580	− 9,420	
(Li_2, Br_2)	159,920	+ 22,700 [2]	182,620
(Ba, Br_2)	x + 23,460 [1]	+ 4,980	x +28,440 [1]
$(Ba, Br_2, 2H_2O)$	x + 32,570	− 4,130	
(Sr, Br_2)	157,700	+ 16,110	173,810
$(Sr, Br_2, 6H_2O)$	181,010	− 7,200	
(Ca, Br_2)	154,920	+ 24,510	179,430
$(Ca, Br_2, 6H_2O)$	180,520	− 1,090	
(Mg, Br_2)	—	—	165,050
(Al_2, Br_6)	239,440	+170,600 [3]	410,040
(Mn, Br_2)	—	—	106,120
(Zn, Br_2)	75,930	+ 15,030	90,960
(Cd, Br_2)	75,200	+ 400	75,640
$(Cd, Br_2, 4H_2O)$	82,930	− 7,290	
(Fe, Br_2)	—	—	78,070
(Co, Br_2)	—	—	72,940
(Ni, Br_2)	—	—	71,820
(Cu_2, Br_2)	49,970	—	—
(Cu, Br_2)	32,580	+ 8,250	40,830
(Pb, Br_2)	64,450	− 10,040	54,410
(Hg_2, Br_2)	50,950	—	—
(Hg, Br_2)	41,880	—	—
$(Hg, Br_2, 2KBr)$	43,110	− 9,750	42,030
(Tl_2, Br_2)	82,590	—	—
(Tl_2, Br_6)	—	—	112,900
(Ag_2, Br_2)	45,400	—	—
(Au_2, Br_2)	− 160	—	—
(Au, Br_3)	+ 8,850	− 3,760	5,090

Reaction.	Heat of formation of the compound.	Heat of solution of the compound.	Heat of formation in aqueous solution.
$(Au, Br_4, H, 5H_2O)$	52,560	− 11,400	41,160
$(Pt, Br_2, 2KBr)$	32,310	− 10,630	21,680
$(Pt, Br_4, 2KBr)$	59,260	− 12,260	47,000
$(Pt, Br_4, 2NaBr)$	46,790	+ 9,990	56,780
$(Pt, Br_4, 2NaBr, 6H_2O)$	65,330	− 8,550	

TABLE 21.

IODIDES.

Reaction.	Heat of formation of the compound.	Heat of solution of the compound.	Heat of formation in aqueous solution.
(K_2, I_2)	160,260 c	− 10,220 c	150,040 c
(Na_2, I_2)	138,160	+ 2,440	140,600
$(Na_2, I_2, 4H_2O)$	148,620	− 8,020	
(Li_2, I_2)	122,430	+ 29,770 [2]	152,200
$(Ba, I_2, 7H_2O)$	x + 4,870 [1]	− 6,850	x − 1,980 [1]
(Sr, I_2)	—	—	143,460
(Ca, I_2)	—	—	149,010
(Al_2, I_6)	140,780	+178,000 [3]	318,780
(Mg, I_2)	—	—	134,630
(Mn, I_2)	—	—	75,700
(Zn, I_2)	49,230	+ 11,310	60,540
(Cd, I_2)	48,830	− 960	47,870
(Fe, I_2)	—	—	47,650
(Co, I_2)	—	—	42,520
(Ni, I_2)	—	—	41,400
(Cu_2, I_2)	32,520	—	—
(Pb, I_2)	39,800	—	—
(Hg_2, I_2)	31,100	—	—
(Hg, I_2)	25,640	—	—
$(Hg, I_2, 2KI)$	28,680	− 9,810	27,540
(Tl_2, I_2)	60,360	—	—
(Ag_2, I_2)	27,600	—	—
(Au_2, I_2)	−11,040	—	—
(Pd, I_2, H_2O)	+18,180	—	—

The thermal values in Tables 20 and 21 are calculated for liquid bromine and solid iodine.

NOTES ON TABLES 19–21.

[1] In the heats of formation of barium compounds the unknown value (Ba, O, H_2O) is represented by x.

[2] Heats of solution of LiBr and LiI according to *Bodisko.*

[3] ,, ,, Al_2Br_6 and Al_2I_6 according to *Berthelot.*

TABLE 22.

CYANIDES.

Reaction.	Heat of formation of the compound.	Heat of solution of the compound.	Heat of formation in aqueous solution.
(K_2, C_2N_2)	130,700 c	−6020 c	124,680 c
(Zn, C_2N_2)	53,400	—	—
(Cd, C_2N_2)	—	—	33,960
(Hg, C_2N_2)	10,280	−2970	7,310
(Ag_2, C_2N_2)	2,790	—	—
$(Zn, C_2N_2, 2KCNAq)$	—	—	62,230
$(Cd, C_2N_2, 2KCNAq)$	—	—	44,750
$(Hg, C_2N_2, 2KCNAq)$	—	—	19,110
$(Ag_2, C_2N_2, 2KCNAq)$	—	—	15,780

TABLE 23.

HYDROGEN METALLO-HALIDES.

Reaction.	Product.	Thermal effect.
$(Hg, Cl_2, 2HClAq)$	H_2HgCl_4Aq	53,110
$(Hg, Br_2, 2HBrAq)$	H_2HgBr_4Aq	43,520
$(Hg, I_2, 2HIAq)$	H_2HgI_4Aq	29,090
$(Sn, Cl_2, 2HClAq)$	H_2SnCl_4Aq	81,000
$(Sn, Cl_4, 2HClAq)$	H_2SnCl_6Aq	156,920
$(Pd, Cl_2, 2HClAq)$	H_2PdCl_4Aq	47,920
$(Pd, Cl_4, 2HClAq)$	H_2PdCl_6Aq	72,940
$(Pt, Cl_2, 2HClAq)$	H_2PtCl_4Aq	41,830
$(Pt, Br_2, 2HBrAq)$	H_2PtBr_4Aq	31,840
$(Pt, Cl_4, 2HClAq)$	H_2PtCl_6Aq	84,620
$(Pt, Br_4, 2HBrAq)$	H_2PtBr_6Aq	57,160
$(Au, Cl_3, HClAq)$	$HAuCl_4Aq$	31,800
$(Au, Br_3, HBrAq)$	$HAuBr_4Aq$	12,790

The heats of neutralization of all these acids are the same, namely, equal to those of hydrochloric, hydrobromic, and hydriodic acids; that is to say, equal to 27,400 c for 2

gram-equivalents of the acid. Hence it follows (see p. 299) that, for example—

$(Pt,Cl_2, 2HClAq) = (Pt, Cl_2, 2NaClAq) = (Pt, Cl_2, MgCl_2Aq)$, etc.

when the bases used for the neutralization are the alkalies, the alkaline earths, or else magnesia.

TABLE 24.

Oxides and Hydroxides.

Reaction.	Thermal effect.	Reaction.	Thermal effect.
(K_2, O, Aq)	164,560 c	$(Bi_2, O_3, 3H_2O)$	137,740 c
(Na_2, O, Aq)	155,260	$(P_2, O_5, 3H_2O)$	400,120
(Li_2, O, Aq)	166,520	$(As_2, O_5, 3H_2O)$	226,180
(Tl_2, O, Aq)	39,160	$(Sb_2, O_5, 3H_2O)$	228,780
(Ba, O, Aq)	$x + 12,260$	(K, O, H, Aq)	116,460
(Sr, O, Aq)	157,780	(Na, O, H, Aq)	111,810
(Ca, O, Aq)	163,330	(Li, O, H, Aq)	117,440
(K_2, O, H_2O)	137,980	(Tl, O, H, Aq)	53,760
(Na_2, O, H_2O)	135,380	(Ba, O_2, H_2, Aq)	$x + 80,620$
(Tl_2, O, H_2O)	45,470	(Sr, O_2, H_2, Aq)	226,140
(Ba, O, H_2O)	x	(Ca, O_2, H_2, Aq)	231,690
(Sr, O, H_2O)	146,140	(Na_2, O)	99,760?
(Ca, O, H_2O)	160,540	(Tl_2, O)	42,240
(Mg, O, H_2O)	148,960	(Hg_2, O)	24,860
(Mn, O, H_2O)	94,770	(Cu_2, O)	40,810
(Zn, O, H_2O)	82,680	(Ag_2, O)	5,900
(Sn, O, H_2O)	68,090	(Ba, O)	$x - 22,260$
(Fe, O, H_2O)	68,280	(Sr, O)	128,440
(Cd, O, H_2O)	65,680	(Ca, O)	145,000
(Co, O, H_2O)	63,400	(Pb, O)	50,300
(Ni, O, H_2O)	60,840	(Cu, O)	37,160
(Cu, O, H_2O)	37,520	(Hg, O)	22,000
(Pd, O, H_2O)	22,710	(As_2, O_3)	154,590
(Pt, O, H_2O)	19,220	(As_2, O_5)	219,380
(Sn, O_2, H_2O)	133,500	(Al_2, O_3, xH_2O)	388,920
(Mn, O_2, H_2O)	116,330	(Fe_2, O_3, xH_2O)	199,150
$(Pd, O_2 H_2O)$	30,430	(Co_2, O_3, xH_2O)	149,380
(Te, O_2, H_2O)	77,180	(Ni_2, O_3, xH_2O)	120,380
$(P_2, O_3, 3H_2O)$	250,320	(Tl_2, O_3, xH_2O)	6,340
$(Sb_2, O_3, 3H_2O)$	167,420	(Au_2, O_3, xH_2O)	−13,190

TABLE 25.

Sulphides (Rhombic Sulphur).

Reaction.	Thermal effect.	Reaction.	Thermal effect.
(H_2, S, Aq)	7,290 c	(K, S, H, Aq)	63,130 c
(K_2, S, Aq)	111,290	(Na, S, H, Aq)	58,480
(Na_2, S, Aq)	101,990	(Li, S, H, Aq)	64,110
(Li_2, S, Aq)	113,250	(Ba, S_2, H_2, Aq)	$x - 25,770$
(Ba, S, Aq)	$x - 40,840$	(Sr, S_2, H_2, Aq)	119,750
(Sr, S, Aq)	104,680	(Ca, S_2, H_2, Aq)	125,300
(Ca, S, Aq)	110,230	(Mg, S_2, H_2, Aq)	110,860
(Mn, S, xH_2O)	44,390	(H_2, S)	2,730
(Zn, S, xH_2O)	39,570	(Tl_2, S)	19,650
(Cd, S, xH_2O)	32,350	(Pb, S)	18,420
(Fe, S, xH_2O)	21,770	(Cu_2, S)	18,260
(Co, S, xH_2O)	19,730	(Hg, S)	6,210
(Ni, S, xH_2O)	17,390	(Ag_2, S)	3,330

TABLE 26.

Reaction of Gaseous Hydracids upon Anhydrous Oxides.

Oxide.	2HCl	2HBr	2HI	2HCN	H_2S
Tl_2O	79,280 c	91,820 c	98,560 c	—	43,040 c
Ag_2O	77,220	90,980	102,140	54,510 c	63,060
Hg_2O	64,710	77,570	86,680	—	—
Cu_2O	49,300	60,640	72,150	—	43,080
HgO	56,840	71,350	84,070	45,910	49,830
PbO	56,830	65,630	69,940	—	33,750
CuO	38,830	46,900	—	—	—

In all these reactions the thermal effect rises from hydrogen chloride to the bromide and iodide, so that hydrogen iodide has the greatest heat of neutralization. This is also observed in the reactions between aqueous solutions of nitrates and of the three halogen acids, and is evident from the figures below,

which represent the heats of reaction on the assumption that the *halides are completely precipitated from solution.*

	2HClAq	2HBrAq	2HIAq
$2TlNO_3Aq$	20,350 c	27,640 c	35,840 c
$2AgNO_3Aq$	31,710	40,220	52,840
$2HgNO_3Aq$	24,290	31,900	42,470
$Hg(NO_3)_2Aq$	15,820	25,080	39,260
$Pb(NO_3)_2Aq$	4,420	7,980	13,750

This behaviour is due to the fact that the heat of precipitation, as will be described later on, is greatest for the iodide, less for the bromide, and least of all for the chloride. In connection herewith is the well-known decomposition of silver chloride by solutions of the bromide or iodide of potassium. The process is attended by a considerable evolution of heat, which is apparent from the difference between the numbers in the table, thus—

$(2AgCl, 2HBrAq) = 40,220 \text{ c} - 31,710 \text{ c} = 8,510 \text{ c}$
$(2AgCl, 2HIAq) = 52,840 - 31,710 = 21,110.$

TABLE 27.

SULPHATES.

Reaction.	Thermal effect.	Heat of solution of the salt.
(K_2, O_2, SO_2)	273,560 c	− 6,380 c
(Na_2, O_2, SO_2)	257,510	+ 460
$(Na_2, O_2, SO_2, 10H_2O)$	276,730	−18,760
(Li_2, O_2, SO_2)	263,090	+ 6,050
(Li_2, O_2, SO_2, H_2O)	265,730	+ 3,410
(Tl_2, O_2, SO_2)	149,900	− 8,280
(Ag_2, O_2, SO_2)	96,200	− 4,480
(Pb, O_2, SO_2)	145,130	—
(Ba, O_2, SO_2)	$x + 120,490$	− 5,580
(Sr, O_2, SO_2)	259,820	—
(Ca, O_2, SO_2)	261,360	+ 4,440
$(Ca, O_2, SO_2, 2H_2O)$	266,100	− 300
(Mg, O_2, SO_2)	231,230	+20,280
(Mg, O_2, SO_2, H_2O)	238,210	+13,300
$(Mg, O_2, SO_2, 7H_2O)$	255,310	− 3,800

Reaction.	Thermal effect.	Heat of solution of the salt.
(Mn, O_2, SO_2)	178,790	+13,790
(Mn, O_2, SO_2, H_2O)	184,760	+ 7,820
$(Mn, O_2, SO_2, 5H_2O)$	192,540	+ 40
(Zn, O_2, SO_2)	158,990	+18,430
(Zn, O_2, SO_2, H_2O)	167,470	+ 9,950
$(Zn, O_2, SO_2, 7H_2O)$	181,680	− 4,260
(Cd, O_2, SO_2)	150,470	+10,740
(Cd, O_2, SO_2, H_2O)	155,160	+ 6,050
$(Cd, O_2, SO_2, \frac{8}{3}H_2O)$	158,550	+ 2,660
$(Co, O_2, SO_2, 7H_2O)$	162,970	− 3,570
$(Ni, O_2, SO_2, 7H_2O)$	162,530	− 4,250
$(Fe, O_2, SO_2, 7H_2O)$	169,040	− 4,510
(Cu, O_2, SO_2)	111,490	+15,800
(Cu, O_2, SO_2, H_2O)	117,950	+ 9,340
$(Cu, O_2, SO_2, 5H_2O)$	130,040	− 2,750

TABLE 28.

NITRATES.

Reaction.	Thermal effect.	Heat of solution of the salt.
(K_2, O_2, N_2O_4)	241,610 c	−17,040 c
(Na_2, O_2, N_2O_4)	225,150	−10,060
(Li_2, O_2, N_2O_4)	225,880	+ 600
(Tl_2, O_2, N_2O_4)	118,950	−19,940
(Ag_2, O_2, N_2O_4)	60,130	−10,880
(Ba, O_2, N_2O_4)	$x + 82,390$	− 9,400
(Sr, O_2, N_2O_4)	222,470	− 4,620
(Ca, O_2, N_2O_4)	219,350	+ 3,950
(Pb, O_2, N_2O_4)	108,110	− 7,610
$(Sr, O_2, N_2O_4, 4H_2O)$	230,150	−12,300
$(Ca, O_2, N_2O_4, 4H_2O)$	230,550	− 7,250
$(Cd, O_2, N_2O_4, 4H_2O)$	123,810	− 5,040
$(Mg, O_2, N_2O_4, 6H_2O)$	213,170	− 4,220
$(Mn, O_2, N_2O_4, 6H_2O)$	156,340	− 6,150
$(Zn, O_2, N_2O_4, 6H_2O)$	140,820	− 5,840
$(Ni, O_2, N_2O_4, 6H_2O)$	123,360	− 7,470
$(Co, O_2, N_2O_4, 6H_2O)$	121,970	− 4,960
$(Cu, O_2, N_2O_4, 6H_2O)$	95,590	−10,710

The reaction thus takes place between the metal, 1 gram-molecule of oxygen, and 1 gram-molecule of N_2O_4 (*non-*

dissociated). Since the heat of formation of non-dissociated N_2O_4 is equal to -2650 c per gram-molecule, we obtain the thermal effect on formation of the nitrates from their elements by adding on -2650 c to the numbers given; and thus find

$$(K_2, N_2, O_6) = 241{,}610 \text{ c} - 2{,}650 \text{ c} = 238{,}960 \text{ c},$$

and similarly for the other nitrates.

TABLE 29.

FORMATION OF SULPHATES AND NITRATES BY THE ACTION OF THE METAL UPON AN AQUEOUS SOLUTION OF THE ACID.

R	(R, O, SO_3Aq)	(R, O, N_2O_5Aq)
K_2	195,850 c	192,100 c
Na_2	186,640	182,620
Li_2	197,810	194,010
Sr	188,490	185,410
Ca	180,409	177,160
Mg	180,180	176,480
Mn	121,250	117,720
Zn	106,090	102,510
Fe	93,200	89,670
Cd	89,880	86,000
Co	88,070	84,540
Ni	86,950	83,420
Pb	—	68,070
Tl_2	70,290	66,540
Cu	55,960	52,410
Hg_2	—	30,650
Hg	—	28,400
Ag_2	20,390	16,780
Al_3^2	150,630	—
Fe_3^2	74,990	—

Thus the tables give the thermal effect of the reaction between the metal, oxygen, and a dilute solution of the acid. These values have a very wide application; for example, by means of them we can calculate the thermal effect on solution of zinc in dilute sulphuric acid with evolution of hydrogen as

$$(Zn, O, SO_3Aq) - (H_2, O) = 106{,}090 \text{ c} - 68{,}360 \text{ c} = 37{,}730 \text{ c},$$

or else the heat of decomposition of a solution of copper sulphate by means of metallic iron—

$$(Fe, O, SO_3Aq) - (Cu, O, SO_3Aq) = 93{,}200 \text{ c} - 55{,}960 \text{ c} = 37{,}240 \text{ c, etc.}$$

TABLE 30.

DITHIONATES.

Reaction.	Thermal effect.	Heat of solution of the salt.
$(K_2, O_2, 2SO_2)$	273,560 c	−13,010 c
$(Na_2, O_2, 2SO_2)$	256,650	− 5,370
$(Na_2, O_2, 2SO_2, 2H_2O)$	262,930	−11,650
$(Ag_2, O_2, 2SO_2, 2H_2O)$	96,090	−10,360
$(Ba, O_2, 2SO_2, 2H_2O)$	$x + 115{,}870$	− 6,930
$(Sr, O_2, 2SO_2, 4H_2O)$	263,610	− 9,250
$(Ca, O_2, 2SO_2, 4H_2O)$	267,870	− 7,970
$(Pb, O_2, 2SO_2, 4H_2O)$	145,490	− 8,540
$(Cu, O_2, 2SO_2, 5H_2O)$	126,250	− 4,870
$(Mg, O_2, 2SO_2, 6H_2O)$	248,410	− 2,960
$(Mn, O_2, 2SO_2, 6H_2O)$	188,600	− 1,930
$(Zn, O_2, 2SO_2, 6H_2O)$	173,850	− 2,240
$(Ni, O_2, 2SO_2, 6H_2O)$	154,790	− 2,420

The thermal effect on formation of salts in aqueous solution is obtained, as is well known, by the addition of the numbers in columns 2 and 3.

TABLE 31.

CARBONATES.

Thermal effect on formation of the salt according to the formula (R, O, CO_2).		Thermal effect on formation of the salt according to the formula (RO, CO_2).	
(K_2, O, CO_2)	184,130 c		
(Na_2, O, CO_2)	175,680		
(Ba, O, CO_2)	$x + 39{,}960$	(BaO, CO_2)	62,220 c
(Sr, O, CO_2)	184,210	(SrO, CO_2)	55,770
(Ca, O, CO_2)	187,520	(CaO, CO_2)	42,520
(Mn, O, CO_2)	113,880		
(Cd, O, CO_2)	84,930		
(Pb, O, CO_2)	72,880	(PbO, CO_2)	22,580
(Ag_2, O, CO_2)	25,960	(Ag_2O, CO_2)	20,060

TABLE 32.

DOUBLE SALTS.

Reaction.	Heat of formation.	Heat of solution.
$(MgSO_4, K_2SO_4)$	3,300 c	+10,600 c
$(ZnSO_4, K_2SO_4)$	4,140	+ 7,910
$(CuSO_4, K_2SO_4)$	20	+ 9,400
$(MnSO_4, K_2SO_4)$	990	+ 6,380
$(MgSO_4, K_2SO_4, 6H_2O)$	23,920	−10,020
$(ZnSO_4, K_2SO_4, 6H_2O)$	23,950	−11,900
$(CuSO_4, K_2SO_4 . 6H_2O)$	22,990	−13,570
$(MnSO_4, K_2SO_4, 4H_2O)$	13,810	− 6,440
$(HgCl_2, 2KCl, H_2O)$	6,130	−16,390
$(HgBr_2, 2KBr)$	1,230	− 9,750
$(HgI_2, 2KI)$	3,040	− 9,810
$(SnCl_4, 2KCl)$	24,160	− 3,380
$(SnCl_2, 2KCl, H_2O)$	4,890	−13,420
$(AuCl_3, HCl, 4H_2O)$	32,130	− 5,830
$(AuBr_3, HBr, 5H_2O)$	35,280	−11,400

Whilst the union of anhydrous sulphates to form a double salt is thus attended by a considerable evolution of heat, there is no heat change on mixing aqueous solutions of these same sulphates, which proves that the double salts are not present as such in aqueous solution. On the other hand, aqueous solutions of the halides interact with considerable evolution of heat; for example—

$(HgCl_2Aq, 2KClAq) = 1920$ c
$(AuCl_3Aq, HClAq) = 4530$
$(AuBr_3Aq, HBrAq) = 7700.$

TABLE 33.

Various other Salts.

Reaction.	Product.	Heat of reaction.	Heat of solution.
(Na_2SO_4, H_2SO_4)	$2NaHSO_4$	13,270 c	$+2 \times$ 1,190 c
(K_2SO_4, H_2SO_4)	$2KHSO_4$	16,640	$-2 \times$ 3,800
(K_2, S_2, O_6)	$K_2S_2O_6$	415,720	− 13,010
(K_2, S_3, O_6)	$K_2S_3O_6$	405,850	− 12,460
(K_2, S_4, O_6)	$K_2S_4O_6$	397,210	− 13,150
$(Na_2, S_2, O_3, 5H_2O)$	$Na_2S_2O_3 . 5H_2O$	265,070	− 11,370
(K, Cl, O_3)	$KClO_3$	95,860	− 10,040
(K, Br, O_3)	$KBrO_3$	84,060	− 9,760
(K, I, O_3)	KIO_3	124,490	− 6,780
(K, Cl, O, Aq)	KClOAq	88,010	—
(Na, Cl, O, Aq)	NaClOAq	83,360	—
(K_2, Mn_2, O_8)	$K_2Mn_2O_8$	389,650	− 20,790
(K_2, Cr_2O_3, O_4)	$K_2Cr_2O_7$	226,440	− 16,700

In calculating the heat of formation of the last-named salt, the chromium is assumed to be present as the violet hydroxide.

TABLE 34.

Thermal Effect of the Reaction between Aqueous Solutions of Nitrates and Sulphuretted Hydrogen.

R	(RN_2O_6Aq, SH_2Aq).
Mn	−12,260 c
Fe	− 6,780
Ni	− 4,960
Co	− 3,740
Zn	− 1,860
Cd	+ 7,120
Pb	+11,420
Tl_2	+14,180
Cu	+16,410
Hg	+38,870
Ag_2	+47,620

The thermal effect is thus positive from cadmium to silver; that is to say, for those nitrates from which the sulphides can be precipitated in dilute, neutral solutions by means of sulphuretted hydrogen; on the other hand, it is negative for the nitrates from which no precipitate is formed by solutions of sulphuretted hydrogen. Zinc forms a transition metal; its sulphides are also precipitated in the presence of acids which have a lower heat of neutralization than nitric acid (for example, acetic and lactic acids), whilst cadmium sulphide, on the contrary, is not precipitated in strongly acid solutions, since the heat of neutralization rises with the concentration.

CHAPTER XII

THE NATURE OF CHEMICAL REACTIONS REGARDED FROM THE DYNAMICAL STANDPOINT

The tendency of matter to attain a state of stable equilibrium is undoubtedly the chief cause of chemical processes. Just as the universal attraction between material particles manifests itself in their tending to approximate their centres of gravity, and thereby to produce the phenomena of pressure, motion, potential or kinetic energy, so also the attraction between the atoms of the molecules tends towards a rearrangement or interchange of the atoms within or between the molecules until a state of stable equilibrium is reached. When this is achieved the chemical reaction between the molecules will be followed by an evolution of energy, which can of course assume different forms, but is most frequently manifested by a rise in temperature; that is to say, heat is evolved.

This tendency of the atoms to assume a state of stable equilibrium may meet with opposition of various kinds. For instance, scarcely any chemical reactions take place between solid substances, since there is neither adequate contact between, nor sufficient motion of, the molecules. This hindrance may be overcome by the action of heat, whereby many of the reacting substances are converted into liquids or gases. Gases, however, do not often interact at ordinary temperatures, but if in such cases the reaction is started, either by heating or in some other manner, it will usually proceed to an end without any further external aid. Hydrogen and oxygen may be induced to react in this way by heating or otherwise, but once started, the reaction goes on of itself until completed; similarly hydrogen and chlorine unite under the influence of light.

Acetylene is stable, but can be detonated by an explosion of mercury fulminate; the acetylene is thus proved to be in a state of unstable equilibrium. In all these instances the reactions proceed to an end with considerable evolution of heat, but they do not take place spontaneously.

Thus we see that the tendency of the atoms to enter into a state of more stable equilibrium is opposed by their tendency to retain the *status quo;* this is a manifestation of the *law of inertia.* An additional amount of energy must therefore be supplied in order to disturb the existing equilibrium of the atoms before they can satisfy their striving after a more stable condition; just as a body standing upon a small base will not overturn of itself, but only when its centre of gravity has been displaced by some external agency so as to lie outside the limits of the base. Thus a number of chemical combinations can also be brought about when the atoms are in the nascent state.

Whilst the action of heat can overcome this opposition to change, and induce a reaction between different substances, a higher temperature will often again resolve the compound formed into its constituents. Thus sulphur dioxide, and similarly also the oxides of barium and mercury, combine with oxygen with rise of temperature, whilst the oxides formed are again decomposed into their original constituents at a still higher temperature. It may often happen that the temperature at which a compound splits up is lower than that at which, under other external conditions, such as, for example, a high pressure, etc., a union of the constituents can be brought about with a large evolution of heat. This is possibly the reason that iodine and oxygen do not unite directly, notwithstanding that each gram-molecule of iodic anhydride is formed with an evolution of 45,030 c.

Although the thermal effect of chemical processes must bear some relation to the degree of stability brought about by the mutual affinities of the atoms, yet nevertheless in a number of cases there is no means of obtaining a trustworthy measure of the magnitude of the affinity itself; for it frequently happens that the constituents are not in the condition in which they

can enter into their compounds, and a considerable amount of energy is therefore required to convert them into the state in which they can take part in the formation of a new molecule. Carbon affords a striking example in this connection, since at ordinary temperatures it cannot enter directly into chemical combination with any other element (with the possible exception of fluorine); a high temperature is therefore necessary in order to provide the large amount of free energy required to produce that change of state in the molecule of solid carbon which enables it to form compounds with the atoms of other molecules (for further details, see Part IV. on the heats of formation of organic compounds).

When the tendency of the atoms to enter into a state of more stable equilibrium is satisfied, there will be a *maximum of free energy;* on the other hand, inertia, or the endeavour to maintain the *status quo*, which tends to oppose any change in the configuration of the molecules, will result in a *minimum of free energy*. Now, since the influence of inertia is weakened by rise of temperature, reactions will often change in character at higher temperatures, in such a manner as to be accompanied by a large evolution of energy. Common experience provides us with a number of such examples as, for instance, in the action of chlorine upon a solution of potassium hydroxide, when, according to the temperature and degree of concentration and with increasing amounts of heat evolved, there will be formed hypochlorous acid, chloric acid, or oxygen (see p. 203); or in the action of zinc upon sulphuric acid, when again according to the temperature and degree of concentration, there will be produced hydrogen, sulphuretted hydrogen, or sulphurous acid, with a progressive rise in the amount of heat evolved (see p. 354).

These two opposing tendencies, namely, the striving to change the configuration of the molecules, and the inertia which resists change, provide us with a valuable means of preparing compounds which cannot be formed by direct methods. Let *AB* represent a compound, the elements of which cannot combine directly owing to insufficient attraction between their affinities, and which will consequently form compounds only by the expenditure

of a large amount of energy; in other words, a considerable absorption of heat. In order to prepare such a compound we therefore select another compound, AC, which can easily be prepared, and is so chosen that the element C has a strong affinity for B. When B acts in this manner upon AC, the affinity between B and C produces a decomposition of AC with the evolution of a large amount of energy, a part of which is absorbed in the formation of the compound AB. Numerous examples might be quoted: thus chlorine monoxide is formed in the reaction between chlorine and mercuric oxide; nitrogen chloride in the reaction between chlorine and ammonia, and so on. In these and similar cases the combined reaction results in an evolution of heat.[1]

To what extent a particular chemical reaction can take place between given substances will therefore, from what has been said above, depend as a rule upon the following conditions:—

1. Whether the necessary rearrangement of the atoms of the molecules can produce a state of more stable equilibrium than that already existing;
2. Whether the inertia of the molecules—that is to say, their opposition to any alteration of the *status quo*, and consequently of their existing configuration—can be overcome in the given case;
3. Whether the reacting substances, at the given temperature and under the other external conditions, are in a suitable condition to take part in the reaction in question; and
4. Whether the possible products of the reaction are stable; that is to say, whether they can exist at the temperature and under the other conditions under which the process is accomplished.

It follows, therefore, from the preceding statements that chemical processes can take place, partly with an *evolution of heat*, partly with an *absorption of heat*. To the first group belong not only the majority of reactions which take place in

[1] See footnote on p. 228.

solution, but also a number of those brought about at high temperatures; amongst the most distinctive of these are the processes of combustion proper. To the other group belong, in the main, only those reactions which are induced by heating a compound so strongly that its stability is destroyed, and it is more or less completely decomposed into its constituents or ultimate elements.

The reason that a substance becomes unstable at a certain temperature is as yet unknown; possibly in the future we may gain some further knowledge in this direction. At present we can only record the facts without explaining them, although certain regularities have been found to occur. Thus all carbonates, with the exception of those of the alkali metals, are decomposed on ignition, and with an absorption of heat. This is also the case with the nitrates, but here, however, the alkali salts are also partially decomposed. In the same way the chlorate, bromate, and iodate of potassium are all decomposed at high temperatures, but whilst in the case of the first two there is an evolution of respectively 9750 c and 11,250 c, potassium iodate, on the other hand, gives a very considerable absorption of heat, namely −44,360 c. From this it is evident that the decomposition of these salts by heating does not bear any relation to the thermal effect of their formation from the corresponding halide and oxygen; since this is negative for two of them, but positive for the third. There must therefore be some other explanation, but what it is is at present unknown. Thus there is still much that is unintelligible in the dynamics of chemical processes, but in the vast majority of chemical reactions, however, it is the "right of the strongest" which holds good to a very marked extent, and this will be proved by numerous examples in the following pages.

Fifty years ago, when I published the results of my earliest work in thermochemistry, namely, "Die Grundzüge eines thermochemischen Systems" in Poggendorff's *Annalen der Physik und Chemie*, vols. 88, 90, 91, and 92 (1853–54), I developed a theory concerning the nature of chemical processes which corresponded in all essentials to that given above. This was the first, and for a series of years the only, attempt to

interpret chemical processes from a dynamical standpoint, and I supported my theory by numerous examples derived from the material then at my disposal.

Thirteen years later Berthelot gave expression to a precisely similar theory, though of a less general nature than my own; and so loudly and continuously did he lay claim to the same that it eventually came to be known by his name. This was the theory of "maximum work," which, however, rapidly lost its significance owing to its one-sided character.

When, during the years 1882–86, I published the collected results of my experiments in thermochemistry, a subject that I had been working at continuously for thirty years, in the well-known *Thermochemische Untersuchungen*, which in its 3500 calorimetric experiments contains over a thousand original determinations connected with this subject, I was able to illustrate the theory that I had previously put forward on the dynamics of chemical processes by means of a large number of examples, for details of which the reader is referred to vol. ii. pp. 468–506, vol. iii. pp. 523–567, and vol. iv. pp. 363–404. The following pages will contain an abstract only of the examples there described, showing how, in agreement with the preceding statements, the course of chemical reactions can be explained from the dynamical standpoint. We shall deal, however, only with those processes of which the thermal values have been given in the preceding chapters (on the non-metals and metals), since the application of the principle mentioned to the interpretation of the heat-phenomena of the so-called organic compounds will be given in Part IV.

A. Hydrides.

The very abundant numerical results dealing with the thermal effect on formation of chemical compounds are, in the preceding chapters, divided into two main groups, one of which comprises the non-metals and the compounds resulting from their interaction, the other the compounds of the metals. Such a division may appear somewhat arbitrary if we consider only the outward appearance of the elements, since many of those

elements which are placed in the group of the non-metals have a metallic exterior, namely, the so-called metalloids (tellurium, arsenic, antimony, etc.); but a surer foundation for this classification is to be found in the chemical properties of the elements. The so-called non-metals are all able to form *gaseous or volatile hydrides*, a property not found in the metals, the hydrides of which, so far as they are known, are solid, non-volatile substances. In the following survey of the heat-phenomena of the elements this division will therefore be retained.

A few only of the non-metals have a strong affinity for hydrogen, namely oxygen, fluorine, chlorine, and bromine, and their combination with this element will therefore take place directly and with evolution of heat; but these hydrides (with the possible exception of hydrogen fluoride) are, however, only formed directly at high temperatures, or in the presence of porous substances which are able to bring about a condensation of the gases. The remaining hydrides, on the other hand, must be formed by indirect methods, as a rule by the so-called double decomposition between a hydrogen compound (for example, an acid or base) and a compound of the non-metal; the first-mentioned group of hydrides can, of course, also be formed in this manner. Thus the hydrides of sulphur, selenium, and tellurium are formed by the action of a compound of the corresponding metal upon hydrogen chloride; ammonia by the action of boron nitride upon potassium hydroxide; the hydrides of boron, phosphorus, arsenic, and antimony by the decomposition of a compound of the corresponding metal by means of water or an acid; the hydrides of chlorine, bromine, and iodine by the action of the corresponding phosphorus compound with water, and so on. In all these cases the reaction takes place by double decomposition; for example—

$$FeS + 2HCl = FeCl_2 + H_2S,$$

and the thermal value, V, of the process follows from the equation

$$(Fe, Cl_2) + (H_2, S) - (Fe, S) - 2(H, Cl) = V.$$

In each of these instances the thermal effect is positive,

and the process will consequently take place with evolution of heat; that is to say, the strongest affinities will be satisfied.

Since the majority of hydrides have their elements but feebly bound, they will also be readily decomposed at higher temperatures; this property is utilized in the well-known test for arsenic and antimony.

In each of the groups of the non-metals the affinity for hydrogen is greatest for the first member, and falls off with an increase of atomic weight. This is particularly noticeable in the case of the monovalent non-metals. The heats of formation per gram-molecule are 37,600 c for hydrogen fluoride (Berthelot), 22,000 c, 8440 c, and −6040 c respectively for the hydrides of chlorine, bromine, and iodine, according to my own researches. For the divalent non-metals the heats of formation of the hydrides are for oxygen 68,360 c, for sulphur 2730 c, for selenium and tellurium strongly negative; similarly for the trivalent non-metals nitrogen is positive (11,890 c), the others are negative, and so on.

This unequal affinity explains the well-known fact that chlorine decomposes the hydrides of bromine and iodine, and that bromine decomposes hydrogen iodide, both in the free state and also in aqueous solution; *the decomposition is in these cases complete*, not partial as in the action of acids upon salts; for each equivalent of chlorine there is liberated an exact equivalent of bromine or iodine.

Since the heat of formation of water is greater than that of the other hydrides (with the exception of hydrogen fluoride), these latter will be decomposed by free oxygen; they are combustible in the widest acceptation of the term; that is to say, they are oxidized with an evolution of heat. Even gaseous hydrogen chloride, with a heat of formation of 44,000 c for 2 gram-molecules of HCl, is decomposed on heating with oxygen into chlorine and water vapour, the heat of formation of which at 100° is 58,060 c (Deacon's chlorine process is based upon this property). When in these cases the amount of oxygen does not exceed that necessary for the oxidation of the hydrogen, the non-metal will be set free, notwithstanding that it is itself combustible; in this manner sulphur, selenium,

phosphorus, arsenic, etc., are liberated by the partial combustion of their hydrides.

When the hydrides of the non-metals are dissolved in water, the conditions are somewhat modified; thus aqueous hydrochloric acid, with a heat of formation of 78,630 c for 2 gram-molecules of HClAq, is not decomposed by oxygen, because the heat of formation of water is only 68,360 c; but solutions of hydrobromic acid, hydrodic acid, and hydrogen sulphide, the heats of formation of which in aqueous solution are respectively 56,760 c, 26,340 c, and 7290 c for 2 gram-molecules, are acted upon by oxygen absorbed from the atmosphere with the liberation of bromine, iodine, and sulphur; the action is naturally smallest in the case of hydrobromic acid. Curiously enough, an aqueous solution of ammonia is not affected by the oxygen absorbed, although its heat of formation in aqueous solution is only 20,320 c for (N, H_3, Aq); but in the gaseous state ammonia is known to be oxidized by free oxygen, for it can be burnt.

Many of the hydrides, as, for example, hydrogen sulphide and hydrogen iodide, owing to their small heats of formation can serve as powerful reducing agents, since the hydrogen in these compounds reacts with much the same strength as free hydrogen towards compounds which contain oxygen, chlorine, and similar elements. Thus sulphuretted hydrogen will reduce aqueous solutions of nitric acid, chromic acid, permanganic acid, ferric salts, etc., to a lower state of oxidation with separation of sulphur; even concentrated sulphuric acid is reduced on warming with evolution of heat and the formation of sulphurous acid and sulphur. The reducing properties of hydrogen iodide are exhibited in the presence of a number of organic compounds containing oxygen; similarly towards solutions of iodic acid, periodic acid, auric chloride, etc.; even sulphuric acid is reduced at ordinary temperatures by means of hydriodic acid.

It is by reason of this last property that hydriodic acid (and also to some extent hydrobromic acid) cannot be prepared, in a similar manner to hydrochloric acid, by the action of concentrated sulphuric acid upon potassium iodide; for the

hydriodic acid liberated reacts immediately with the sulphuric acid forming sulphurous acid, water, and free iodine, and this process, similarly to those previously described, takes place with a large evolution of heat, which, according to the tables, is in the case of the last-mentioned reaction

$$(H_2, O) - (SO_2, O, H_2O) - 2(H, I) = R,$$
$$68{,}360\text{ c} - 53{,}480\text{ c} \quad + 12{,}080\text{ c} = 26{,}960\text{ c.}$$

Hydriodic acid, therefore, *reduces* sulphuric acid to sulphur dioxide and water with the separation of iodine; but in the presence of a large amount of water the reverse process takes place, since an aqueous solution of sulphurous acid is oxidized by means of free iodine with the formation of sulphurous acid and hydrogen iodide. The thermal effect of this reaction is

$$-(H_2, O) + (SO_2Aq, O) + 2(H, I, Aq) = Q,$$
$$-68{,}360\text{ c} + 63{,}630\text{ c} \quad + 26{,}340\text{ c} \quad = 21{,}610\text{ c.}$$

Thus in this case also the process is attended by a large evolution of heat. Now, since both (SO_2Aq, O) and $2(H, I, Aq)$ decrease in magnitude with a reduction of the amount of water, the value of Q will be lower the smaller the amount of water present, and from the heats of dilution already given for the two acids (see Tables 4 and 7) the thermal value, Q, will become zero when there are only about six molecules of water present for each molecule of iodine. If the amount of water be still further diminished the process is reversed, since the hydriodic acid has a reducing action on the sulphuric acid formed. These two reciprocal processes may be easily illustrated in the following manner: Concentrated sulphuric acid is added to a strong solution of potassium iodide, when the first process takes place, iodine is separated and sulphurous acid is formed. The liquid is then diluted with water, when it again becomes colourless; this is the other phase of the process in which hydriodic acid is regenerated. This is one example amongst a number of processes in which the amount of water present determines the character of the reaction. In a similar manner hydriodic acid is known to be formed

from phosphorus, iodine, and water, with the formation of phosphorous acid, whilst with smaller amounts of water the phosphorous acid is reduced by hydriodic acid to phosphine (phosphonium iodide).

All these processes take place with evolution of heat; that is to say, the strongest affinities assert themselves. The heat of formation of marsh gas, CH_4, is also positive (21,710 c); but it is formed directly only in very small quantity, owing to the resistance offered by carbon to the formation of compounds. By the simultaneous action, however, of carbon disulphide and sulphuretted hydrogen upon metallic copper, marsh gas is formed with evolution of heat.

B. Oxides.

The majority of elements combine directly with oxygen, and the combination is always attended by an evolution of heat; but it is only exceptionally that the reaction between the element and oxygen takes place at ordinary temperatures; as a rule it must be brought about by heating. Oxidation will therefore only take place provided the resulting oxide can exist at the temperature necessary to the process of oxidation. An instructive example in this connection is the relation of mercury to oxygen. The metal is not acted upon by oxygen at ordinary temperatures, but must first be heated almost to the boiling-point, when the oxidation proceeds with a very considerable evolution of heat, namely about 22,000 c; but the mercuric oxide formed is again decomposed into the metal and oxygen at a temperature which lies 150° above the boiling-point of mercury. The oxidation can therefore take place only within the narrow interval of about 150°.

This property explains how it is that a substance does not always unite directly with oxygen, notwithstanding that the union would take place with an evolution of heat. Iodine, platinum, palladium, and silver belong to this group of substances. The direct formation of iodic anhydride (I_2O_5) would

involve an evolution of 45,030 c for each gram-molecule of I_2; but the reaction does not take place, probably because the compound is not stable at the temperature at which oxidation is possible. The same holds good for silver and platinum, the oxides of which are not formed directly, although their formation would be accompanied by an evolution of respectively 5900 c and 19,000 c. In the case of palladium the temperatures at which oxidation proceeds, and at which the oxide is again decomposed, must lie very near together; since palladium is oxidized by heating in the air. That silver can be directly oxidized at low temperatures is evident from the fact that finely divided silver, on shaking up with a very dilute solution of sulphuric acid, takes up oxygen from the air and forms silver sulphate.

The heats of oxidation of the different metals are very unequal. With respect to the thermal effect on taking up equal amounts of oxygen, magnesium heads the list with a value of 148,000 c for each gram-atom of oxygen; next follow the metals of the alkalies and alkaline earths, whilst the remaining metals arrange themselves in the following order: Mn—Zn—Fe—Sn—Cd—Co—Ni—Pb—Tl—Cu—Hg—Pd — Pt — Ag — Au. The thermal value for gold is negative, namely, −4400 c for a gram-atom of oxygen; it is the only metal of which the heat of oxidation is negative.

The stability of an oxide at high temperatures must in all probability stand in close relationship to its heat of formation. Amongst the oxides of the metals named, the last five only are completely decomposed into their elements on heating. The heat of formation of HgO is 22,000 c, of PtO and PdO of about equal magnitude, whilst that of Ag_2O, on the other hand, is only 5900 c; a corresponding amount of energy will accordingly be set free on decomposition.

A partial reduction also takes place when the higher oxides are not stable at high temperatures; in this way sulphur trioxide is decomposed into sulphur dioxide and oxygen with an absorption of 32,160 c; similarly arsenic oxide is reduced to arsenious oxide with an absorption of $2 \times 32{,}350$ c. The explanation of this decomposition is as yet quite unknown.

The heats of oxidation of the non-metals are likewise very unequal. The *maximum* value is reached in the case of phosphorus, and amounts to 74,000 c for 1 gram-atom of oxygen when phosphoric anhydride is formed; it is, however, *negative* for chlorine, bromine, and nitrogen. With the exception of these three substances (and of iodine, the relation of which to oxygen has already been described) the non-metals are combustible; that is to say, they unite with oxygen with a large evolution of heat (but in general, the reaction must be started by heating).

When an element can form several oxides, the composition of the products of the reaction will be dependent upon the stability of the oxides at the temperature of combustion. Thus on burning sulphur, selenium, and arsenic in free oxygen the lower oxides SO_2, SeO_2, and As_2O_3 are formed, since the higher oxides are not stable at the temperature of combustion; on the other hand, phosphorus and carbon form the higher oxides P_2O_5 and CO_2 on active combustion; but if the oxidation takes place in the presence of an insufficient amount of oxygen, or at a lower temperature, the lower oxides can likewise be formed, since these are also stable at high temperatures.

On oxidation of an element by heating in oxygen, that oxide is usually formed which, with the same amount of the substance, will give the greatest amount of heat; but if a lower or a higher oxide is stable at the temperature of the reaction, it also is either wholly or in part formed. This is as a rule, however, due to a secondary reaction brought about by the action of that element which is present in excess.

Those elements of which the heats of oxidation are negative can naturally not combine directly with oxygen; the oxides must be formed in an indirect manner, or by supplying the necessary energy in some other way, as, for example, by means of electricity or of a very high temperature. Amongst the non-metals this holds good for chlorine, bromine, and nitrogen. Thus the oxides of chlorine and bromine can be formed by the action of the elements upon certain oxides (for example, HgO), for the electropositive element of which they

have a strong affinity, and a sufficient amount of energy is thereby set free to bring about the formation of the oxide in question. In the case of nitrogen the oxidation is produced, as is well known. by the aid of electrical energy.

C. Chlorides.

Chlorine has a strong affinity for all the elements with the exception of fluorine, oxygen, and nitrogen, and its compounds can also usually be formed directly. As this formation can most frequently take place at ordinary temperatures, the formation of the chlorides does not as a rule present any difficulty; carbon, and possibly also platinum, are the only instances in which there is not direct union with chlorine, although the formation of the chlorides takes place with an evolution of heat.

The compounds of chlorine with oxygen or nitrogen, which are produced with absorption of heat, must necessarily be formed indirectly by the method already described on p. 332.

The chlorides of the non-metals are (with the exception of the chlorides of carbon) all decomposed by water at ordinary temperatures; and there is formed a solution of hydrochloric acid and of the acid or hydroxide of the element originally present as chloride. In all cases the decomposition is attended by a large evolution of heat, which approaches its maximum, namely 123,440 c, for 1 gram-molecule of PCl_5. The amount of heat evolved bears a certain relation to the molecular weight of the chloride; for it is evident from the following table that *in each group of analogous chlorides the evolution of heat on hydrolysis decreases as the molecular weight increases.* Thus the heat of decomposition is smaller for selenious chloride than for sulphur chloride, and smaller for arsenious chloride than for phosphorous chloride, etc.

THERMAL EFFECT ON DECOMPOSITION OF THE CHLORIDES BY WATER.

Reaction.	Thermal effect.	Reaction.	Thermal effect.
$(S_2Cl_2 : Aq)$	35,400 c	$(PCl_3 : Aq)$	65,140 c
$(Se_2Cl_2 : Aq)$	16,200	$(AsCl_3 : Aq)$	17,580
$(SeCl_4 : Aq)$	30,370	$(SbCl_3 : Aq)$ [1]	8,910
$(TeCl_4 : Aq)$ [2]	20,340	$(BiCl_3 : Aq)$ [1]	7,830
$(CCl_4 : Aq)$	95,150 [3]	$(SbCl_3 : Aq)$ [2]	7,730
$(SiCl_4 : Aq)$	69,260	$(BiCl_3 : Aq)$ [2]	−6,350
$(TiCl_4 : Aq)$	57,870	$(PCl_5 : Aq)$	+123,440
		$(SbCl_5 : Aq)$	35,200

The property described, namely, that the heats of reaction in each group of analogous chlorides decrease with a rise in the atomic weight of the non-metal, receives confirmation in every case.

The thermal effect, V, due to the decomposition of the chlorides by water can be expressed by the following equation—

$$V = (R, O_m, Aq) - (R, Cl_{2m}) + 2m(H, Cl, Aq) - m(H_2, O).$$

The difference between the last two terms is a constant, namely—

$$2m(H, Cl, Aq) - m(H_2, O) = m \times 10{,}270 \text{ c},$$

and the value of the first two terms will therefore be

$$(R, O_m, Aq) - (R, Cl_{2m}) = V - m \times 10{,}270 \text{ c}.$$

Substituting for V the values given in the table above, we find that *the last-named difference is a positive magnitude for all*

[1] The observed heat of reaction when there is a partial decomposition with the formation respectively of $Sb_4O_5Cl_2$ and BiOCl.

[2] This value represents the thermal effect on complete decomposition (see p. 237).

[3] The thermal effect calculated for the decomposition into CO_2Aq and $4HClAq$.

the chlorides investigated with the exception of the chlorides of tellurium, antimony, and bismuth; we therefore have

$$(Te,\ O_2,\ H_2O) - (Te,\ Cl_4) = -\quad 200\ c$$
$$\tfrac{1}{2}(Sb_2,\ O_3,\ H_2O) - (Sb,\ Cl_3) = -\ 2{,}680$$
$$\tfrac{1}{2}(Bi_2,\ O_3,\ H_2O) - (Bi,\ Cl_3) = -21{,}760.$$

Now these three chlorides, $TeCl_4$, $SbCl_3$, and $BiCl_3$, are *the only instances amongst the chlorides of the non-metals investigated which are not completely decomposed by water*, and there are therefore grounds for the assumption that in order that the hydrolysis should be complete the following conditions must be satisfied, namely—

$$(R,\ O_m,\ H_2O) - (R,\ Cl_{2m}) > O.$$

The extent of the partial decomposition of the three chlorides mentioned above will also bear a close relation to the magnitude of this difference. For of 1 gram-molecule of $TeCl_4$, 0·972 gram-molecules are decomposed, and the difference is -200 c; whereas of 1 gram-molecule of $SbCl_3$ and of 1 gram-molecule of $BiCl_3$, $\frac{5}{6}$ and $\frac{2}{3}$ of a gram-molecule are respectively decomposed, whilst the differences are -2680 c and $-21{,}760$ c. Thus the greater the negative value of the difference described, the less will be the hydrolytic action of the water.

The fact that CCl_4 undergoes no appreciable hydrolysis must be due to some special cause; in all probability there is insufficient contact. I have observed a similar relation between sulphuryl chloride SO_2Cl_2, and water; we can shake up the two together for hours and still not produce a complete decomposition; but if some solid iodine be added to the mixture the sulphuryl chloride loses its spheroidal condition, and the decomposition then proceeds very rapidly; but in the case of carbon tetrachloride, however, there seem to be still other hindrances at work.

The *chlorides of the metals* all have positive heats of formation; that of auric chloride being the lowest, namely, 22,820 c for 1 gram-molecule of $AuCl_3$; they can therefore all be formed also by direct methods. Platinum certainly seems to form an

exception; for although the heat of formation of the chloride is very considerable, its direct formation has not hitherto been effected.

The chlorides are for the most part soluble in water, and the solution is accompanied *partly* with an *evolution of heat*, as, for instance, when the chloride is able to form a hydrated compound—thus $CaCl_2$, $CuCl_2$, $AuCl_3$, etc., are dissolved with evolution of heat, and their corresponding hydrates are, as is well known, $CaCl_2 . 6H_2O$, $CuCl_2 . 2H_2O$, and $AuCl_3 . 2H_2O$; *partly*, on the other hand, with *absorption of heat*, provided they do not form compounds with water, as is the case for KCl, $PbCl_2$, $AuBr_3$, and the sparingly soluble compounds of the formula R_2Cl_2, etc. Likewise the hydrated chlorides which contain the full number of water molecules that they are able to combine with will, almost without exception, dissolve with absorption of heat.

A comparison between the heats of formation of the chlorides of the metals and those of the corresponding hydroxides leads to interesting results.

It has been shown above that in the case of the non-metals the difference between the heats of formation of the chlorides and of the corresponding hydroxides is negative, thus

$$(R, Cl_{2n}) - (R, O_n, nH_2O) < O,$$ valid for the non-metals;

an exception being found for tellurium, antimony, and bismuth. But with the metals *the opposite relation holds good, since the chlorides have a greater heat of formation than the corresponding oxides or hydroxides*, and therefore

$$(R, Cl_2) - (R, O, H_2O) > O,$$ valid for the metals.

To this group belong also tellurium, antimony, and bismuth, which are undoubtedly non-metals, notwithstanding their metallic appearance. The only exceptions amongst the chlorides of the metals investigated were aluminium chloride and stannic chloride; stannous chloride, on the other hand, was in agreement with the given rule. This relation seems all the more remarkable when we remember that the decomposition of the chlorides of the non-metals by means of water gives rise to two acids which do not interact, whilst in the corresponding

reaction with the chlorides of the metals an acid and a base are formed which can again enter into combination.

The difference observed in the magnitude of the thermal effect for the chlorides and the corresponding hydroxides would therefore appear to point to some characteristic difference between the metals and the non-metals, which can be expressed in the following manner: *The heats of formation of the chlorides of the metallic elements are greater than those of the corresponding hydroxides, when the latter are formed from the metal, oxygen, and water, whilst the heats of formation of the chlorides of the non-metallic elements are lower than those of the corresponding hydroxides.* Amongst all the chlorides investigated the only exception found was that of aluminium chloride, together with some of the higher chlorides; but these also are almost completely decomposed on solution in water.

D. Bromides and Iodides.

The chlorides of the metals have in all cases a greater heat of formation than the bromides, and these again have a greater heat of formation than the iodides; but in the remainder of their properties the halogens are in very close agreement. In accordance with their thermochemical properties iodides are decomposed by bromine, and both iodides and bromides by chlorine; this decomposition is complete, and is attended by an evolution of heat.

When those halides which are insoluble in water, as, for example, Ag_2Cl_2, Tl_2Cl_2, etc., are acted upon by an aqueous solution of the halide of another metal, an interchange takes place between the elements, provided that the halogen element of the insoluble halide has a lower atomic weight than the halogen in solution. Thus silver chloride is decomposed by a solution of either the bromide or iodide of potassium with the formation of the respective bromide or iodide of silver; the thermal effect of the reaction can be expressed in the following manner:—

$$2AgCl, 2KIAq) = \begin{cases} 2(KOHAq, HClAq) - 2(KOHAq, HIAq) \\ +(Ag_2O, 2HIAq) \quad -(Ag_2O, 2HClAq). \end{cases}$$

Now, since the first difference is approximately equal to zero, and the second is, on the other hand, strongly positive (namely 63,720 c $-42{,}580$ c), the reaction will take place with an evolution of 21,140 c. The reaction is therefore dependent upon that difference between the heats of reaction of the three halide acids with silver and other analogous oxides which was described on p. 323.

E. Halides of the Metals.

The halides of certain of the metals, as, for instance, Pt, Pd, Au, Hg, etc., combine with the corresponding halogen acid to form acids soluble in water, the properties of which remind us in many respects of hydrochloric, hydrobromic, and hydriodic acids. The formation of these acids is accompanied by an evolution of heat, notwithstanding that the reacting constituents are already present in aqueous solution; so that, for example, from the facts previously given in describing the various metals, the thermal effect of the following processes will be

$$(AuCl_3Aq, HClAq) = 4530 \text{ c}$$
$$(AuBr_3Aq, HBrAq) = 7770$$
$$(HgCl_2Aq, 2HClAq) = 1920.$$

In these instances there is therefore an actual reaction taking place between the two solutions, whilst solutions of, for example, $MgCl_2$, $FeCl_2$, $CuCl_2$, etc., are without action upon aqueous solutions of hydrochloric acid. In all these cases the heat of reaction is greatest for the iodine compounds, lower for those of bromine, and lowest of all for the chlorine compounds.

The majority of these acids are not known in the free state, but only as crystalline hydrates, such as $H_2PtCl_6 . 6H_2O$, $HAuCl_4 . 4H_2O$, $HAuBr_4 . 5H_2O$, $HHgBr_3 . 4H_2O$, etc.; the last-mentioned acid is decomposed in aqueous solution to form $HgBr_2$ and H_2HgBr_4 (see also "Tin," p. 271). All these acids have the same heat of neutralization as an equivalent amount of hydrochloric acid, and, similarly to it, they form

soluble salts with the majority of the metals; the Pb, Hg, and Ag salts are, however, insoluble.

On neutralization with sodium hydroxide these acids form salts which are not as a rule decomposed by an excess of the alkali; only when the solution is heated to the boiling-point does decomposition take place, with separation of the metallic hydroxide. This is the case, for example, with $NaAuCl_4$ and Na_2PtCl_4; but Na_2PtCl_6, on the other hand, is not decomposed on boiling with an equivalent amount of a caustic soda solution.

It is worthy of note that the oxides of those metals which form compounds with the halogen acids give only a very small thermal effect (heat of neutralization) when acted upon by nitric acid in aqueous solution, and many of them are even insoluble in this acid, whereas they all react vigorously with hydrochloric acid. Coupled with this is the well-known fact that the addition of hydrochloric acid does not cause the precipitation of silver chloride from a solution which contains mercuric hydroxide, silver hydroxide, and nitric acid, until the mercuric nitrate has first been converted into chloride.

F. Behaviour of the Metals in the Presence of Water and of Acids.

The behaviour of the metals in the presence of water and of acids serves to illustrate the principle that I have laid down, namely, that the tendency of matter to attain a state of stable equilibrium is the cause of chemical processes, which must therefore be attended by a liberation of energy, usually manifested in the form of heat.

It has already been stated that with regard to the magnitude of their affinity towards oxygen the metals can be arranged in the following order: the metals of the alkaline earths (including MgO) and of the alkalies, and then Mn, Zn, Fe, Sn, Cd, Co, Ni, Pb, Tl, Cu, Hg, Pd, Pt, Ag, and Au. The affinity is positive for all the metals with the single exception of gold; and the magnitude of the thermal effect on formation of

their oxides or hydroxides determines their behaviour towards water or the acids.

If the heat of oxidation of a metal is greater than 68,360 c for each gram-atom of oxygen—that is to say, greater than the heat of formation of water—the metal will, as a consequence, *decompose water with evolution of hydrogen.* From the figures in Table 24 it is evident that this is the case for the alkali metals and alkaline earths, together with Mg, Mn, and Zn, all of which react with water to form hydroxides. The velocity with which the reaction takes place is, however, very different, and depends partly upon the greater or lesser affinity of the metal for oxygen, and partly upon the solubility of the hydroxide formed in water. Whilst in the case of potassium the reaction is very violent, it is scarcely appreciable for manganese and zinc, since the surface of the metal is coated by the insoluble hydroxide formed; it is only when the metal is pulverized, or freed from the coating of hydroxide, that the action becomes vigorous.

Whilst the heat of formation of liquid water is 68,360 c, the value amounts only to 58,060 c for 1 gram-molecule of water vapour at 100°, and the limiting values for the *metals which are able to decompose water vapour* thus come to lie between those of nickel and lead, for which the heats of formation of the oxides are respectively 60,840 c and 50,300 c. In addition to the metals which decompose liquid water, it was therefore to be expected that Sn, Fe, Cd, Co, and Ni would also decompose water vapour with evolution of heat, and this has been confirmed by experiment. The oxides of the remaining metals, namely, Pb, Tl, Cu, Hg, Pd, Pt, Ag, and Au, of which the heats of oxidation are less than 58,060 c, are, on the other hand, reduced to the metallic state by means of hydrogen, and this also takes place with evolution of heat. Similarly the higher oxides, such as MnO_2 and CrO_3, are reduced by hydrogen to the lower oxides with evolution of heat.

A remarkable property is found to exist in the case of nickel, cobalt, and iron, since these metals decompose water vapour, whilst their oxides are also reduced by hydrogen. The heats of formation of these oxides, which vary from 60,280 c to

68,280 c, approximate very closely to that of water vapour, namely 58,060 c; thus the thermal effect is but small in both cases, and the course of the process must to a great extent depend upon the relative amounts of the reacting substances.

The behaviour of the metals in the presence of acids is of great interest, since it affords numerous examples by means of which "the right of the stronger" has been found to hold good throughout the course of chemical reactions. Hydrochloric, sulphuric, and nitric may be regarded as the most important acids, since by the action of metals they form salts, most of which are readily soluble. The thermal effect is of course dependent upon the character of the reaction, the simplest relation being found in the action of hydrochloric acid upon the metals.

(*a*) *Hydrochloric acid* dissolves a number of metals with evolution of hydrogen; the hydrochloric acid is thus decomposed with the formation of a chloride of the metal. The necessary condition for the reaction will therefore be that the thermal effect should be positive. Now, since the process corresponds to the equation

$$(M : 2\,HClAq) = (M,\ Cl_2,\ Aq) - (H_2,\ Cl_2,\ Aq),$$

where M represents the metal, the condition of the reaction will be that

$$(M,\ Cl_2,\ Aq) > (H_2,\ Cl_2,\ Aq).$$

The heat of formation of 2 gram-molecules of hydrochloric acid in very dilute aqueous solution is 78,630 c; this value decreases as the concentration of the acid increases, and for a very concentrated acid amounts only to about 60,000 c (see p. 80). If now we compare with this the numbers contained in Table 19, which are the heats of formation of the chlorides of the metals in aqueous solution, we shall find that for 1 gram-molecule of Cl_2 the value is less than 78,630 c in the case of gold, platinum, silver, mercury, lead, and copper, all of which metals are known to be insoluble in dilute hydrochloric acid. For tin the heat of formation is 81,140 c, and it is much higher for the other metals, namely, 112,840 c for zinc, 202,340 c

for potassium. *Tin* thus forms a transition metal; the heat of formation of stannous chloride is but little removed from 78,630 c, and the metal is acted upon to only a small extent by dilute acid; but with increased concentration of the acid its heat of formation falls off, so that the affinity to be overcome must also become less, and the solution of tin in strong hydrochloric acid will therefore take place with a very large evolution of heat. *Lead* also gives rise to lead chloride and hydrogen when acted upon by concentrated acid; the heat of formation of lead chloride in aqueous solution is 75,970 c, and this very greatly exceeds the heat of formation of concentrated hydrochloric acid, which, as has been shown above, can fall to about 60,000 c. Even *copper* dissolves in concentrated hydrochloric acid with *evolution of hydrogen and the formation of cuprous chloride*, of which the heat of formation is 65,750 c; and, here again, the process takes place with evolution of heat; but owing to the small difference in the heats of formation of the two substances the reaction only proceeds vigorously when the liquid is warmed, and more particularly if we make use of finely divided copper.

When a metal is dissolved in hydrochloric acid, it is always the lower chloride which is formed; thus tin, copper, and iron give stannous, cuprous, and ferrous chlorides, and not the higher chlorides, because the former process takes place with the greater evolution of heat. It is also found that the higher chlorides of these metals are reduced to the lower state of oxidation by the action of the metal, and this process is likewise attended by an evolution of heat.

(*b*) *Sulphuric acid in dilute solution* shows similar properties to hydrochloric acid, and forms sulphates with evolution of heat. The limit for the two groups of metals is essentially the same, *copper* alone amongst the metals which give off hydrogen forms an exception, since the limit is determined by the equation

$$(M,\ O,\ SO_2Aq) > (H_2,\ O,\ SO_3Aq);$$

that is to say, the heat of formation of the sulphate must be greater than that of 1 gram-molecule of water, *i.e.* 68,360 c, whilst the value for copper is only 55,960 c.

Thallium is on the border-line, with a heat of formation of 70,290 c for the sulphate; and the solution of the metal in very dilute acid is therefore also very slow; but with increased concentration of the sulphuric acid solution the thermal value rises, and at the same time the velocity of solution increases. When *zinc* is dissolved in dilute sulphuric acid the heat evolved will, according to Table 29, amount to 37,730 c.

If the sulphuric acid solution is very concentrated, the reaction takes place in other ways; the most familiar instance is the solution in concentrated acid with *evolution of sulphur dioxide*. The reaction is expressed by the following equation:—

$$R + 2H_2SO_4 = RSO_4 + SO_2 + 2H_2O,$$

and the thermal value of the process for 1 gram-atom of a divalent metal (R) will be

$$(R,\ O_2,\ SO_2) + 2(H_2,\ O) + a + b - 2(H_2,\ O_2,\ SO_2) = V.$$

a is the heat of vaporization of 1 gram-molecule of SO_2 (6200 c), which must be added on, since the sulphur dioxide is eventually evolved as a gas—this is a secondary effect which should have no influence on the thermal value of the process; b is the thermal effect due to the reaction between the water formed and the free acid present. If the latter be taken as 1 gram-molecule, b will be equal to 9400 c. The remaining values will be found in the tables referred to. On inserting these we obtain

$$(R,\ O_2,\ SO_2) - 91{,}360 \text{ c} = V;$$

that is to say, the thermal effect of the process will be positive, provided the heat of formation of the sulphate is greater than 91,360 c; and this is the case for all the metals with the exception of gold and platinum. For silver sulphate the heat of formation is 96,200 c, so that silver, like the remainder of the metals, forms a sulphate when acted upon by concentrated sulphuric acid. The thermal value for zinc would be 67,630 c (see Table 27).

If we assume that the same process takes place with zinc and very dilute sulphuric acid, the thermal value will be

42,460 c, which is thus 4730 c greater than when zinc dissolves in dilute acid with evolution of hydrogen, and yet the former process does not take place. The formation of sulphur dioxide is hindered by the tendency of the molecules to retain their original configuration; it is only when this opposition to any change of the *status quo* is removed, by raising the temperature and concentration, that the reaction proceeds. But there is nevertheless a third reaction, intermediate between the other two, namely, the *solution of zinc with evolution of hydrogen sulphide.*

This reaction occurs when on evaporation of the acid a certain concentration has been reached, and takes place according to the equation

$$4Zn + 5H_2SO_4Aq = 4ZnSO_4Aq + H_2S;$$

the process is attended by an evolution of heat amounting to about 57,900 c for each gram-atom of zinc.

The reaction between zinc and sulphuric acid can thus proceed in three different ways, characterized respectively by the evolution of hydrogen, hydrogen sulphide, and sulphur dioxide. The thermal effect in the three cases is

$Zn + H_2SO_4Aq = ZnSO_4Aq + H_2$ thermal effect 37,730 c
$4Zn + 5H_2SO_4Aq = 4ZnSO_4Aq + H_2S$ „ 4 × 57,900
$Zn + 2H_2SO_4 = ZnSO_4 + SO_2 + 2H_2O$ „ 67,630.

Thus the processes follow on, one after the other, with rise of concentration and of temperature, and with an increasing thermal effect; and at the same time a larger proportion of the original molecules undergo a change in constitution. Whilst in the first case the whole of the SO_4 radicals retain their form unchanged, in the second one-fourth of them are decomposed, and in the last example one-half. We have here an excellent illustration of how the tendency to maintain the *status quo* is overcome by means of a greater concentration and a higher temperature.

In connection with this I may mention that sulphuric acid in dilute solution is not reduced either by hydrogen or by hydrogen sulphide, notwithstanding that such a process would be attended by an evolution of heat; it is only at great

concentration, and on heating strongly, that the action can be brought about.

(*c*) *Nitric acid* behaves in essentially the same way as sulphuric acid, but the solution of the metal with evolution of hydrogen is, however, but rarely observed, since the hydrogen has a reducing action on the nitric acid, giving rise to nitrous oxides, hydroxylamine, and ammonia. Usually, therefore, the reaction proceeds with the formation of the nitrate, and at the same time nitrogen or its oxides are evolved. When the resulting product is nitric oxide (*NO*), the thermal value of the process for each gram-atom of a divalent metal dissolved in *very dilute nitric acid* will be

$$(R,\ O,\ N_2O_5Aq) - \tfrac{1}{3}(2NO,\ O_2,\ Aq) = V.$$

The last process corresponds to an evolution of $3 \times 24{,}320$ c, and therefore those metals of which the heat of formation of the nitrate is attended by a greater thermal effect than 24,320 c for each gram-atom of metal are dissolved by very dilute acid. We see from Table 29 that this is the case for all the metals with the exception of silver, for which the value amounts only to 16,780 c when very dilute acid is used. But if the concentration of the acid be increased, the magnitude V will also increase; for whilst the first term of the equation above is increased, the second has a lower value; V will therefore be positive for an acid corresponding to a formula of approximately $HNO_3 . 3H_2O$. Moreover, at a higher temperature and concentration the reaction can assume a different character, since the molecule *NO* is then decomposed with evolution of heat, so that nitrogen appears as one of the products of the reaction. Whilst at low temperatures copper dissolves in dilute nitric acid with an evolution of 28,000 c, this value, provided the temperature of the liquid be raised, can only rise to about 50,000 c, since the nitric acid would then be reduced to nitrogen.

As a metal which can decompose water, zinc on treatment with very dilute nitric acid will form zinc nitrate and hydrogen, with a thermal effect of 34,150 c; but nascent hydrogen has a reducing action on nitric acid, whereby water

and ammonium nitrate are formed; and by this means the evolution of heat is increased by 47,160 c for each gram-atom of zinc, so that it reaches a total of 81,310 c. Thus on placing a bright strip of zinc in very dilute nitric acid, we notice that the metal dissolves without a trace of any gas being given off, whilst a heavy liquid settles around the metal.

(*d*) *Aqua regia* behaves in much the same way as chlorine, since hydrochloric and nitric acids decompose each other in concentrated solutions, forming chlorine and nitrosyl chloride, in which the chlorine is so feebly bound that it can be decomposed even by gold and platinum. Since *aqua regia* behaves in almost exactly the same way as chlorine, it will react with the metals, giving rise to the *higher* chlorides, such as $AuCl_3$, H_2PtCl_6, $CuCl_2$, SnCl , Fe_2Cl_6, etc., whilst hydrochloric acid, on the other hand, forms the lower chlorides, such as Cu_2Cl_2, $SnCl_2$, $FeCl_2$ since the process will produce a considerable amount of energy which decomposes the hydrochloric acid.

(*e*) *The precipitation of a metal* from solution by means of another metal follows the given rule; that is to say, the strongest affinities always prevail, and the process is accompanied by an evolution of heat, as shown by the values in Table 29. In accordance with experience the order will be silver, mercury, copper, lead, cadmium, zinc, etc., and the first-mentioned metals will be precipitated by those which follow; it must, however, be remembered that many of the metals, such as zinc, aluminium, and magnesium, have so strong an affinity for oxygen that they can be oxidized at the expense of water, after which they combine with the acid of the salt present in solution, so that the metal of the latter is precipitated as oxide and not as the metal. A well-known instance of this is the action between zinc and a neutral solution of an iron salt.

G. Decomposition of Oxides by means of Chlorine and Carbon or Carbon Monoxide.

Amongst the numerous chemical processes which take place with evolution of heat may be mentioned the formation of the chlorides of aluminium, silicon, and titanium from their

oxides by the simultaneous action of carbon and chlorine. It is evident from the thermal values given for these processes that neither chlorine nor carbon alone can decompose the oxides mentioned with evolution of heat,[1] and, as we know, decomposition does not take place. On the other hand, if the two substances act simultaneously upon the oxide, the sum of the affinities—that is, the affinity of chlorine for the electropositive element of the oxide and of carbon for oxygen—is greater than the affinities of the constituents of the oxide for each other, and as a result the decomposition is accompanied by an evolution of heat. In addition to the chloride the products of the reaction will, according to the conditions, consist of the monoxide or dioxide of carbon. If we represent the oxide by R_aO_n, the thermal value of the process will correspond to one of the following equations:—

$$V = (R_a, Cl_{2n}) - (R_a, O_n) + \tfrac{n}{2}(C, O_2)$$
$$V = (R_a, Cl_{2n}) - (R_a, O_n) + n(C, O),$$

according to whether the monoxide or dioxide is formed. Now, since $\frac{1}{2}(C,O_2)$ is equal to 48,480 c and (C, O) is equal to 29,000 c, whilst the difference $(R_a, Cl_{2n}) - (R_a,O_n)$ is equal to $-n \times 24{,}360$ c, to $-n \times 19{,}165$ c, and to $-n \times 22{,}320$ c, respectively, for silicon, titanium, and aluminium, the process will in both cases be attended by a large evolution of heat; for example, for aluminium—

$$V = 3 \times 48{,}480 \text{ c} - 3 \times 22{,}320 \text{ c} = 78{,}480 \text{ c}$$
$$V_1 = 3 \times 29{,}000 \quad - 3 \times 22{,}320 \quad = 20{,}040$$

This method of forming the chlorides was first mentioned by H. C. Örsted; at a later date he modified the method, in that carbon monoxide was employed in place of carbon (Riban, *Bul. soc. chim.* 39, 14). The heat of oxidation of carbon monoxide (CO, O) is equal to 67,960 c, so that we have, for example, for aluminium—

$$V_2 = 3 \times 67{,}960 \text{ c} - 3 \times 22{,}320 \text{ c} = 136{,}920 \text{ c}.$$

[1] At the temperature of the electric furnace, silica and carbon yield silicon (translator).

The thermal effect will therefore be much greater than when carbon is used, and the process will also proceed at a lower temperature than in the first case.

H. Decomposition at High Temperatures.

It is a matter of common experience that a number of compounds which are very stable at low temperatures are decomposed when subjected to strong heating. The decomposition is in many cases accompanied by a large evolution of heat, as, for example, with a number of explosive substances, and the process is then in accordance with the majority of the reactions already described, in which the tendency of matter to attain a state of more stable equilibrium produces a reaction with evolution of energy. As an example we may mention the decomposition by heat of potassium chlorate, potassium bromate, and silver oxalate; for the first two reactions the thermal effect is comparatively small, but it may nevertheless be sufficient to raise the substance to a red heat; in the last case the decomposition takes place explosively, since the silver oxalate is converted into metallic silver and carbon dioxide with a very large evolution of heat.

In the majority of cases, however, the decomposition of a compound at high temperatures is attended by absorption of heat; but it is often apparent that the temperature which brings about the decomposition stands in some definite relation to the magnitude of the affinity which has to be overcome. Thus the absorption of heat on decomposition of the following carbonates to carbon dioxide and the oxide of the metal is

Lead carbonate	22,580 c
Calcium carbonate	42,520
Strontium carbonate	55,770
Barium carbonate	62,220

Amongst these carbonates that of lead is decomposed at a moderately low temperature, the calcium and strontium salts require a higher temperature, and barium carbonate is decomposed only by very strong ignition.

The same relations are observed in the decomposition of the corresponding nitrates to RO, O, and N_2O_4, which are attended by an absorption of respectively

57,810 c, 74,350 c, 94,030 c, 104,650 c;

so that here again the temperature necessary to the decomposition rises with the amount of heat absorbed in the decomposition; but in the case of the nitrates the temperature is lower than for the corresponding carbonates, notwithstanding that the heats of formation of the former salts are greater than those of the latter.

A number of metallurgical processes are also attended by a large absorption of heat, as, for example, in the separation of Na, Mn, Zn, Cd, Sn, Fe, etc., from their oxides or salts by fusion with charcoal. In order to decompose the oxides of Cd, Sn, and Fe, about 66,000 c are required for each gram-atom of oxygen; whilst carbon on uniting with a gram-atom of oxygen evolves only 29,000 c or 48,480 c, according to whether the monoxide or the dioxide is formed, a considerable amount of heat is consequently taken up during the course of the reaction.

There are therefore a great many chemical processes which proceed with absorption of heat; but the chief examples of these must be sought in reactions which take place between dry substances at high temperatures. On the other hand, it would appear as if those reactions which take place in solution, and similarly also a large number of those which proceed without the action of water, or between dry substances, follow the given rule, according to which the chemical process takes place with evolution of energy; that is, in accordance with general dynamical principles. At present we have no knowledge of the conditions of stability of a chemical compound at high temperatures. But although there are many deviations from the dynamical principles laid down for chemical processes, which have not yet been explained, there are nevertheless a great many instances in which the theory is supported by so large a number of facts that, notwithstanding the deficiencies indicated, it still affords an important means of grouping

the majority of chemical processes from a common standpoint, and, at least apparently, explains their course on a dynamical basis; that is to say, as the result of the tendency of matter to attain a state of stable equilibrium.

I. Dependence of the Thermal Effect upon the Molecular Weights of the Reacting Substances.

Allied elements form, as is well known, compounds of analogous composition and with common properties, such as solubility in water or in acids, volatility, stability at high temperatures, and so on; properties which, however, change somewhat with the atomic weights of the elements in the compound. Thus the solubility in water falls off from lead chloride to lead bromide, and from the bromide to the iodide, when the atomic weight of the varying element of the compound increases; and similarly also for the sulphates of the alkaline earths and many other compounds. In a like manner the volatility falls off with a rise of atomic weight in the series of the higher chlorides of phosphorus, arsenic, and antimony, or in the sulphurous, selenious, and tellurous acid series; whilst the stability of the carbonates at high temperatures increases in the alkaline earth series, Mg, Ca, Sr, and Ba, as the atomic weight rises.

Similar regularities are also noted with respect to the magnitude of the thermal effect which accompanies those chemical processes in which analogous compounds are formed from allied substances. It has already been mentioned that the thermal value of the formation of analogous halogen compounds, with hydrogen or a metal as one of the constituents, is greatest for the chlorides, less for the bromides, and least of all in the case of the iodides; and here also the thermal effect falls off as the atomic weight of the halogen increases. The same decrease in thermal effect with a rise of atomic weight is observed on formation of the oxygen compounds of chlorine and bromine, sulphur and selenium, phosphorus and arsenic. In each of these groups the thermal value is greatest for the first member; but we now observe the following

peculiarity, namely, that the third member belonging to each of the three groups, *i.e.* I, Te, and Sb, produces a greater thermal effect than the second on formation of the corresponding oxygen compound (see p. 217). We may therefore conclude that the affinity between the first two members in every group is greater than that between either of these and the third member.

There is at present no satisfactory answer to the question as to the relation between the thermal effect and the atomic weight, although some such connection may be observed in the material under consideration; I shall therefore restrict myself to pointing out this connection in the case of one group of elements, namely, the metals of the alkaline earths, Mg, Ca, Sr, and Ba.

The relation of the compounds of magnesium, calcium, strontium, and barium to water shows very plainly the dependence of the affinity upon the molecular weight of the substance. Arranged in order of the magnitude of their atomic weights, the elements named form the following series :—

Mg	Ca	Sr	Ba
24	40	88	137

and the physical and chemical properties of their compounds vary in precisely the same order, as does also the thermal effect attendant upon their analogous reactions.

The oxides of these metals show different degrees of affinity towards water; for magnesium hydroxide is decomposed at quite a low temperature, calcium hydroxide at a red heat, whilst the hydroxides of strontium and barium are decomposed only after a prolonged heating at a far higher temperature. Precisely the same relation holds for the *heats of hydration of the oxides*, namely—

$$(MgO, H_2O) = \text{about } 3{,}000 \text{ c}$$
$$(CaO, H_2O) = \text{,, } 15{,}540$$
$$(SrO, H_2O) = \text{,, } 17{,}700$$
$$(BaO, H_2O) = \text{,, } 22{,}260.$$

The *hydroxides* are not all equally soluble in water; magnesium hydroxide is almost insoluble, calcium hydroxide very

sparingly soluble, strontium hydroxide dissolves more easily, and barium hydroxide is the most soluble of all. The heats of solution of the hydroxides were found to be

$$(Mg(OH)_2, Aq) = \text{about } 0 \text{ c}$$
$$(Ca(OH)_2, Aq) = 2{,}790$$
$$(Sr(OH)_2, Aq) = 11{,}640$$
$$(Ba(OH)_2, Aq) = 12{,}260.$$

Thus the *heats of hydration of the oxides of the metals*, and similarly also the *heats of solution of the hydroxides*, increase with the molecular weight of the compound.

The *halides* of these metals behave in the opposite manner, for the affinity of these compounds for water, and likewise the thermal effect of their combination with the latter—that is, their *heats of hydration*—are in each series of halides *smaller the greater is the molecular weight of the compound.* Amongst the anhydrous chlorides $MgCl_2$ is the most strongly hygroscopic, and $BaCl_2$ the least so; and whilst the chlorides of the first three metals take up six molecules of water of crystallisation, $BaCl_2$ can combine only with two molecules; the affinity for water thus decreases with the rise of atomic weight. *The heats of hydration and of solution* of these chlorides are as follows:—

$$(MgCl_2, 6H_2O) = 32{,}970 \text{ c} \qquad (MgCl_2, Aq) = 35{,}920 \text{ c}$$
$$(CaCl_2, 6H_2O) = 21{,}750 \qquad (CaCl_2, Aq) = 17{,}410$$
$$(SrCl_2, 6H_2O) = 18{,}640 \qquad (SrCl_2, Aq) = 11{,}140$$
$$(BaCl_2, 2H_2O) = 7{,}000 \qquad (BaCl_2, Aq) = 2{,}070.$$

This comparison shows that the heats both of hydration and of solution *decrease regularly when the molecular weight of the chloride increases.* A similar relation is found for the other halogen compounds of these metals, and also for a number of their salts, such as the nitrates and dithionates. Thus the heats of hydration of the nitrates of calcium and strontium are

$$(CaN_2O_6, 4H_2O) = 11{,}200 \text{ c}$$
$$(SrN_2O_6, 4H_2O) = 7{,}670,$$

so that the heats of hydration of the nitrates also decrease with a rise of molecular weight; this behaviour is in accordance with the fact that magnesium nitrate takes up six molecules

of water, the nitrates of strontium and calcium only five, whilst barium nitrate is anhydrous.

The heats of solution of the nitrates and dithionates also follow the same rule; the values are as follows:—

$(CaN_2O_6, Aq) = +3950$ c $(CaS_2O_6 . 4H_2O, Aq) = -7970$ c
$(SrN_2O_6, Aq) = -4620$ $(SrS_2O_6 . 4H_2O, Aq) = -9250$
$(BaN_2O_6, Aq) = -9400$ ..

so that here again the heats of solution decrease with rise of molecular weight.

A comparison between the heats of solution of the chloride, bromide, and iodide of the same metal shows the following characteristic property, namely, that in the Li, Na, Ca, Sr, and Ba series the value is lowest for the chloride, higher for the bromide, and highest of all for the iodide; thus for equivalent quantities:—

	Li_2	Na_2	Ca	Sr	Ba
Cl_2	16,880 c	−2360 c	17,410 c	11,140 c	2070 c
Br_2	22,700	− 380	24,510	16,110	4980
I_2	29,780	+2440	27,690	—	—

But the reverse is the case in the Zn, Cu, Cd, Pb, and Au series, since the chlorides of these metals have the greatest, the bromides a lower, and the iodides the smallest heats of solution, as shown in the following table:—

	Zn	Cu	Cd	Pb	$Au\frac{2}{3}$
Cl_2	15,630 c	11,080 c	3010 c	− 6,800 c	+2970 c
Br_2	15,030	8,250	440	−10,040	−2510
I_2	11,310	—	−960	—	—

This difference in behaviour in the heats of solution of the two series of halogen compounds can hardly be accidental, but must certainly be due to some unknown cause.

PART IV

ORGANIC SUBSTANCES

CHAPTER XIII

HEATS OF COMBUSTION OF VOLATILE ORGANIC SUBSTANCES

A. Methods of Investigation and Numerical Results.

The investigation of the thermal effect on formation of organic substances from their elements presents especial difficulties; for only extremely few organic compounds can be directly so formed, and then it is usually under conditions which are not adapted to thermochemical research. The heats of formation of some substances can be determined indirectly in solution, by decomposition with other substances of which the heats of formation are already known. Thus, for example, the heats of formation of zinc methyl, acetyl chloride, chloral, etc., can be derived from the thermal effect of their decomposition by means of water or of the solution of an alkali, provided the heats of formation of the products of the reaction, *i.e.* of methane, acetic acid, chloroform, or formic acid, etc., have already been determined. In a like manner the heats of neutralization of the organic acids, alkaloids, and amines can be measured in solution; but the fundamental values, such as the heats of formation of the hydrocarbons, alcohols, acids, amines, nitriles, etc., cannot be measured either by such direct or indirect methods.

At the present time there is no satisfactory process known for the measurement of these values, other than the estimation of the heats of combustion; that is to say, the thermal effect

due to the complete oxidation of the substances, by means of which carbon dioxide, water, nitrogen, hydrogen chloride, etc., are formed. The procedure is therefore precisely similar to that employed for the quantitative determination of the composition of organic substances; for in the so-called elementary analysis the percentage composition of the substance is calculated from a knowledge of the weights of water, carbon dioxide, etc., which are formed on complete oxidation of an organic compound, but the heat of oxidation is not taken into consideration. For thermochemical purposes, on the other hand, it is simply the heat of combustion which is the subject of investigation, whilst the percentage composition of the substance is taken as known; and the weight of the fully oxidized substance is deduced from the weight of the products of combustion, provided it is not already known. If now from the formula

$$f.\,C_aH_{2b}O_c$$

we calculate the thermal effect due to the complete oxidation of 1 gram-molecule of the compound $C_aH_{2b}O_c$, we obtain the equation

$$(C_a,\ H_{2b},\ O_c) + f.\,C_aH_{2b}O_c = a(C,\ O_2) + b(H_2,\ O);$$

that is to say, the sum of the thermal value due to the formation of the compound from its elements, C_a, H_{2b}, and O_c, together with the heat of combustion of the compound, is equal to the thermal effect on direct formation of the products of combustion, aCO_2 and bH_2O.

The thermal value on formation of a compound, $C_aH_{2b}O_c$, can therefore be represented by the following general equation :—

$$(C_a,\ H_{2b},\ O_c) = a(C,\ O_2) + b(H_2,\ O) - f.\,C_aH_{2b}O_c.$$

Now, if the heats of formation of carbon dioxide and of water are known, the heat of formation of the substance will follow from its heat of combustion.

The heats of combustion of the majority of substances (with the exception of formic acid and carbonyl chloride) are very much greater than their heats of formation, often even several times as great. Thus the heat of combustion of

1 gram-molecule of CH_4 is 211,930 c, whilst the calculated heat of formation is 21,750 c—that is, only about one-tenth the value; for 1 gram-molecule of C_6H_{14} the heat of combustion is 999,200 c, whilst its heat of formation is only 61,080 c, or about one-sixteenth as great. Whence it follows that the investigations must be so arranged as to attain the *greatest possible accuracy in the determination of the heats of combustion;* for the whole error in this number will naturally fall upon the far smaller value, which represents the heat of formation. A difference of $\frac{1}{4}$ per cent. in determining the heat of combustion of C_6H_{14} amounts to 2498 c, and this will also affect the calculated heat of formation *i.e.* 61,082 c; but in the latter case the error will amount to 4 per cent.

Hence it also follows *that the investigation must be limited to compounds containing a small number of carbon atoms in the molecule*, for otherwise the uncertainty will be far too great, even although the combustion experiments are carried out with the utmost care, since the direct measure of the heat of combustion can rarely attain a greater accuracy than $\frac{1}{4}$ per cent. We must therefore lay special stress on the necessity of carrying out a large number of combustion experiments, and of obtaining an accurate determination for the first member in each series of homologous compounds; for, as we shall see later, the heats of combustion of the higher members of the series can be derived from those of the lower members. My researches were consequently restricted to compounds containing not more than six atoms of carbon in the molecule, except in the case of aromatic compounds, of which the first member already contains six atoms of carbon, when compounds containing as many as nine atoms of carbon were investigated.

The heats of combustion are naturally dependent upon the state of aggregation, and we must therefore always start with the substance in the same condition if we wish to establish a comparison between the heats of combustion of a number of different compounds. I have confined my researches to volatile or gaseous organic substances, and determined *directly the heats of combustion of all the substances examined in the state of gas or vapour.*

The investigation comprised in all 120 organic substances, belonging to the following main groups: *hydrocarbons*, *compounds of chlorine, bromine, and iodine*, *alcohols*, *acids*, *aldehydes*, *ketones*, *oxides of alcohol radicals*, *sulphur compounds*, *esters*, *amines*, *nitro-compounds*, and allied substances.

In *Thermochemische Untersuchungen*, vol. iv. pp. 7–219, I have given an accurate description of the details of this very extensive research, including the construction of the apparatus used, the carrying out of the experiments, an account of all the direct observations, and of the general equations used in calculating the experimental results, as well as of the degree of purity of the substances under investigation; in short, everything that is necessary for the complete interpretation of each separate experiment, so that the reader may be in a position to judge for himself as to the reliance which may be placed upon the experimental results. In the present volume I shall confine myself to an account of the numerical results obtained, and of the theoretical conclusions that may be deduced therefrom.

B. Tabular Comparison of the Numerical Results of the Experimental Investigations.

In the following tables I have collected together the numerical results of my determinations of the heats of combustion of organic substances, and also, derived therefrom, the thermal effect on formation of the compounds from their elements. The *first* and *second* columns contain the names of the substances and their constitutional molecular formulæ. The *third* and *fourth* columns give the heats of combustion, which in the case of non-gaseous bodies is given both at the boiling-point and also in the state of gas or vapour at 18°. In each case it is assumed that the products of combustion are cooled to 18°, and that consequently carbon dioxide and nitrogen appear as gases—water, on the other hand, as a liquid. If a compound contains elements other than carbon, hydrogen, oxygen, and nitrogen, such as chlorine, bromine,

iodine, or sulphur, the state of aggregation of these substances assumed in the calculations is given in the tables.

The *fifth* column gives the heats of formation of the products of the combustion; that is to say, the amount of heat which is evolved by the elements of the compound when they are burned in the free state, as, for instance, carbon to the dioxide, and hydrogen to water. *The heat of combustion of carbon is taken as* 96,960 c *for each gram-atom of carbon, this being the heat of combustion of amorphous carbon. The heat of formation of water is* 68,360 c *per gram-molecule.*

The *sixth* and *seventh* columns contain the heats of formation of the substances in the state of gas or vapour at 18°. This value is calculated from the heats of combustion according to the equation already given—

$$(C_a, H_{2b}, O_c) = a(C, O_2) + b(H_2, O) - f(C_aH_{2b}O_c).$$

The values calculated in this manner are the heats of formation at *constant pressure.* External conditions, however, exercise a certain influence on these values, since the products formed usually occupy a smaller volume than the sum of the volumes of the constituent elements. Thus 2 gram-molecules of hydrogen are required for the formation of 1 gram-molecule of CH_4; this corresponds, therefore, to a decrease in volume of 1 gram-molecule of hydrogen, or of 22,340 cubic centimeters at 0° and 760 mm. pressure. Such a diminution of volume will result in the evolution of 543 c at 0°, which corresponds to 580 c at 18°. If now from the heat of formation of the compound we subtract 580 c for each gram-molecular volume which has disappeared, we obtain the *heat of formation at constant volume.* It is this value which is given in the seventh column of the following tables:—

TABLE 35.

HYDROCARBONS.

Combustion : $C_aH_{2b} + (2a + b)O = aCO_2 + bH_2O$.

Compound.	Molecular formula.	Heat of combustion of the vapour at the boiling-point.	Heat of combustion of the gas at 18°.	Heat of formation of the products.	Heat of formation of the compound at constant pressure.	Heat of formation of the compound at constant volume.
PARAFFINS.						
Methane	CH_4	—	211,930 c	233,680 c	21,750 c	21,170 c
Ethane	C_2H_6	—	370,440	399,000	28,560	27,400
Propane	C_3H_8	—	529,210	564,320	35,110	33,370
Trimethylmethane	$CH(CH_3)_3$	—	687,190	729,640	42,450	40,130
Tetramethylmethane	$C(CH_3)_4$	—	847,110	894,960	47,850	44,950
Diisopropyl	$(CH)_2 . (CH_3)_4$	—	999,200	1,060,280	61,080	57,600
AROMATIC HYDROCARBONS.						
Benzene	C_6H_6	801,160	799,350	786,840	−12,510	−13,670
Toluene	$C_6H_5 . CH_3$	958,950	955,680	952,160	− 3,520	− 5,260
Mesitylene	$C_6H_3(CH_3)_3$	1,289,330	1,282,310	1,282,800	+ 490	− 2,410
Pseudocumene	$C_6H_3(CH_3)_3$	1,288,770	1,281,510	1,282,800	+ 1,310	− 1,590
UNSATURATED HYDROCARBONS.						
Ethylene	C_2H_4	—	333,350	330,640	− 2,710	− 3,290
Propylene, normal	$CH_2 : CH . CH_3$	—	492,740	495,960	+ 3,220	+ 2,060
Trimethylene	C_3H_6	—	499,430	495,960	− 3,470	− 4,630
Isobutylene	$CH_2 : C : (CH_3)_2$	—	650,620	661,280	+10,660	+ 8,920
Isoamylene	$C_2H_4 : C : (CH_3)_2$	—	807,630	826,600	+18,970	+16,650
Diallyl	$C_3H_5 . C_3H_5$	—	932,820	923,560	− 9,260	−11,580
Acetylene	$C : CH$	—	310,050	262,280	−47,770	−47,770
Allylene	$CH \vdots C . CH_2$	—	467,550	427,600	−39,950	−40,530
Dipropargyl	$C_3H_3 . C_3H_3$	—	882,880	786,840	−96,040	−97,200

TABLE 36.

Halogen Compounds.

In calculating the heats of combustion and of formation of the bromides and iodides, the products are assumed to be *gaseous* bromine or iodine, and similarly in the case of chlorine. The formula for the combustion will therefore be—

$$C_aH_bI + \left(2a + \frac{b}{2}\right)O = aCO_2 + \frac{b}{2}H_2O + I_{gas} \text{ (or } Br_{gas} \text{ or } Cl_{gas}).$$

Compound.	Molecular formula.	Heat of combustion		Heat of formation of the products.	Heat of formation of the compound	
		of the vapour at the boiling-point.	of the gas at 18°.		at constant pressure.	at constant volume.
Methyl chloride	CH_3Cl	—	176,950 c	199,500 c	22,550 c	21,970 c
Ethyl chloride	C_2H_5Cl	—	344,110	364,820	30,710	29,550
Propyl chloride	C_3H_7Cl	493,070 c	492,380	530,140	37,760	36,020
Isobutyl chloride	C_4H_9Cl	651,600	650,090	695,460	45,370	43,050
Monochlorethylene	C_2H_3Cl	—	298,340	296,460	− 1,880	− 2,460
Monochlorpropylene	C_3H_5Cl	453,470	453,370	461,780	+ 8,410	+ 7,250
Allyl chloride	C_3H_5Cl	445,230	454,680	461,780	+ 7,100	+ 5,940
Phenyl chloride	C_6H_5Cl	767,490	763,880	752,660	−11,220	−12,380
Ethylene chloride	$CH_2Cl \cdot CH_2Cl$	297,830	296,360	330,640	+34,280	+33,120
Ethylidene chloride	$CH_3 \cdot CHCl_2$	277,290	296,410	330,640	34,230	33,070
Chloracetol	$CH_2 \cdot CCl_2 \cdot CH_3$	455,370	453,880	495,960	42,080	40,340
Carbonyl chloride	$COCl_2$	—	41,820	96,960	55,140	54,850
Chloroform	$CHCl_3$	107,830	107,030	131,140	24,110	23,530
Monochlorethylene chloride	$C_2H_3Cl_3$	264,900	262,480	296,460	33,980	32,820
Tetrachlormethane	CCl_4	77,220	75,930	96,960	21,030	20,450
Tetrachlorethylene	C_2Cl_4	—	195,070	193,920	− 1,150	− 1,730
Methyl bromide	CH_3Br	—	184,710	199,500	+14,790	+14,210
Ethyl bromide	C_2H_5Br	342,240	341,820	364,820	23,000	21,840
Propyl bromide	C_3H_7Br	500,710	499,290	530,140	30,850	29,110
Allyl bromide	C_3H_5Br	463,360	462,120	461,780	− 340	− 1,500
Methyl iodide	CH_3I	196,580	196,080	199,500	+ 3,420	+ 2,840
Ethyl iodide	C_2H_5I	355,030	353,730	364,820	11,090	9,930

TABLE 37.

ETHERS AND ACETALS.

Combustion : $C_aH_{2b}O_n + (2a + b - n)O = aCO_2 + bH_2O$.

Compound.	Molecular formula.	Heat of combustion		Heat of formation of the products.	Heat of formation of the compound	
		of the vapour at the boiling-point.	of the gas at 18°.		at constant pressure.	at constant volume.
Ethylene oxide	$CH_2 . O . CH_2$	—	312,550 c	330,640 c	18,090 c	17,220 c
Dimethyl ether	$CH_3 . O . CH_3$	—	349,360	399,000	49,640	48,190
Methylethyl ether	$CH_3 . O . C_2H_5$	—	505,870	564,320	58,450	56,420
Diethyl ether	$C_2H_5 . O . C_2H_5$	660,200 c	659,600	729,640	70,040	67,430
Methylallyl ether	$CH_3 . O . C_3H_5$	628,010	627,200	661,280	34,080	32,050
Diallyl ether	$C_3H_5 . O . C_3H_5$	914,270	911,100	923,560	12,460	9,850
Methylpropargyl ether . .	$CH_3 . O . C_3H_3$	—	603,830	592,920	−10,910	−12,360
Anisol	$CH_3 . O . C_6H_5$	941,960	936,300	952,160	+15,860	+13,830
Methylal	$CH_2(OCH_3)_2$	476,850	476,080	564,320	88,240	85,920
Methyl orthoformate . . .	$CH(OCH_3)_3$	602,630	599,180	729,640	130,460	127,270

TABLE 38.

ALCOHOLS.

Combustion: $C_aH_{2b}O + (2a + b - 1)O = aCO_2 + bH_2O$.

Compound.	Molecular formula.	Heat of combustion		Heat of formation of the products.	Heat of formation of the compound	
		of the vapour at the boiling-point.	of the gas at 18°.		at constant pressure.	at constant volume.
Methyl alcohol	$CH_3 . OH$	182,920 c	182,230 c	233,680 c	51,450 c	50,580 c
Ethyl alcohol	$C_2H_5 . OH$	341,790	340,530	399,000	58,470	57,020
Propyl alcohol	$C_3H_7 . OH$	500,780	498,630	564,320	65,690	63,660
Isopropyl alcohol	$(CH_3)_2 . CHOH$	495,050	493,320	564,320	71,000	68,970
Isobutyl alcohol	$(CH_3)_2 . CH . CH_2OH$	661,490	658,490	729,640	71,150	68,540
Trimethyl carbinol . . .	$(CH_3)_3COH$	643,500	641,340	729,640	88,300	85,690
Isoamyl alcohol	$(CH_3)_2 . C_2H_2 . CH_2OH$	824,570	820,070	894,960	74,890	71,700
Dimethylethyl carbinol . .	$(CH_3)_2 . C . C_2H_5 . OH$	813,740	810,450	894,950	84,510	81,320
Allyl alcohol	$C_3H_5 . OH$	466,640	464,760	495,960	31,200	29,750
Propargyl alcohol	$C_3H_3 . OH$	433,090	431,100	427,600	− 3,500	− 4,370
Phenyl alcohol	$C_6H_5 . OH$	774,430	768,760	786,840	+18,080	+16,630
Ethylene glycol	$C_2H_4(OH)_2$	302,770	298,110	399,000	100,890	99,150

TABLE 39.

Aldehydes and Ketones.

Combustion : $C_aH_{2b}O + (2a + b - 1)O = aCO_2 + bH_2O$.

Compound.	Molecular formula.	Heat of combustion of the vapour at the boiling-point.	Heat of combustion of the gas at 18°.	Heat of formation of the products.	Heat of formation of the compound at constant pressure.	Heat of formation of the compound at constant volume.
Acetic aldehyde	$CH_3 . COH$	281,940 c	281,900 c	330,640 c	48,740 c	47,870 c
Propionic aldehyde . . .	$C_2H_5 . COH$	441,470	440,720	495,960	55,240	53,790
Isobutyric aldehyde . . .	$C_3H_7 . COH$	601,210	599,900	661,280	61,340	59,310
Dimethyl ketone	$CH_3 . CO . CH_3$	438,180	437,250	495,960	58,710	57,260
Methylpropyl ketone . . .	$CH_3 . CO . C_3H_7$	757,220	754,190	826,600	72,410	69,400

TABLE 40.

Acids and Acid Anhydrides.

Combustion : $C_aH_{2b}O_c + (2a + b - c)O = aCO_2 + bH_2O$.

Compound.	Molecular formula.	Heat of combustion of the vapour at the boiling-point.	Heat of combustion of the gas at 18°.	Heat of formation of the products.	Heat of formation of the compound at constant pressure.	Heat of formation of the compound at constant volume.
Formic acid	$H . CO_2H$	70,750 c	69,390 c	165,320 c	95,930 c	95,350 c
Acetic acid	$CH_3 . CO_2H$	227,650	225,350	330,640	105,290	104,130
Propionic acid	$C_2H_5 . CO_2H$	390,080	386,510	495,960	109,450	107,710
Acetic anhydride	$(C_2H_3O)_2O$	464,270	460,070	592,920	132,850	130,820

TABLE 41.

ESTERS.

Combustion : $C_aH_{2b}O_c + (2a + b - c)O = aCO_2 + bH_2O$.

Compound.	Molecular formula.	Heat of combustion		Heat of formation of the products.	Heat of formation of the compound	
		of the vapour at the boiling-point.	of the gas at 18°.		at constant pressure.	at constant volume.
Methyl formate	$CH_2 . CHO_2$	241,620 c	241,210 c	330,640 c	89,430 c	88,270 c
Methyl acetate	$CH_2 . C_2H_2O_2$	400,330	399,340	495,960	96,720	94,980
Ethyl formate	$C_2H_5 . CHO_2$	401,100	400,060	495,960	95,900	94,160
Methyl propionate	$CH_2 . C_3H_5O_2$	556,130	553,950	661,280	107,330	105,010
Ethyl acetate	$C_2H_5 . C_2H_3O_2$	548,670	546,570	661,280	114,710	112,390
Propyl formate	$C_3H_7 . CHO_2$	560,970	558,800	661,280	102,480	101,160
Methyl isobutyrate	$CH_2 . C_4H_7O_2$	719,970	716,940	826,600	109,660	106,760
Isobutyl formate	$C_4H_9 . CHO_2$	723,200	719,900	826,600	106,700	103,800
Allyl formate	$C_3H_5 . CHO_2$	529,980	527,900	592,920	65,020	63,280
Dimethyl carbonate . . .	$(CH_3)_2CO_3$	359,930	357,570	495,960	138,390	136,360
Diethyl carbonate	$(C_2H_5)_2CO_3$	678,960	674,100	826,600	152,500	149,310
Ethyl nitrate	$C_2H_6 . NO_2$	325,690	324,040	364,820	40,780	38,750

TABLE 42.

MERCAPTANS, SULPHIDES, SULPHOCYANIDES, ISOSULPHOCYANIDES, ETC.

Combustion: $C_aH_bSN + \left(2a + \frac{b}{2} + 2\right)O = aCO_2 + \frac{b}{2}H_2O + SO_{2gas} + N.$

Compound.	Molecular formula.	Heat of combustion of the vapour at the boiling-point.	Heat of combustion of the gas at 18°.	Heat of formation of the products.	Heat of formation of the compound at constant pressure.	Heat of formation of the compound at constant volume.
Hydrogen sulphide . . .	H_2S	—	136,710 c	139,440 c	2,730 c	2,730 c
Methyl hydrosulphide . .	$CH_3 . SH$	298,850 c	298,810	304,760	5,950	5,370
Ethyl hydrosulphide . . .	$C_2H_5 . SH$	456,060	455,650	470,080	14,430	13,270
Dimethyl sulphide	$(CH_3)_2 . S$	457,760	457,350	470,080	12,730	11,570
Diethyl sulphide	$(C_2H_5)_2 . S$	774,820	772,170	800,720	28,550	26,230
Thiophene	C_4H_4S	612,210	610,640	595,640	−15,000	−15,580
Methyl sulphocyanide . .	$CH_3 . S . NC$	401,750	398,950	367,540	−31,410	−31,990
Methyl isosulphocyanide . .	$CH_3 . N . CS$	394,590	392,060	367,540	−24,520	−25,100
Allyl mustard oil	$C_3H_5 . N . CS$	679,920	675,360	629,820	−45,540	−46,700
Carbon disulphide	CS_2	265,490	265,130	239,120	−26,010	−25,430
Carbonyl sulphide	COS	—	131,010	168,040	+37,030	+37,320

TABLE 43.

CYANOGEN, HYDROGEN CYANIDE, NITRILES AND AMINES.

Combustion : $C_aH_bN_c + \left(2a + \frac{b}{2}\right)O = aCO_2 + \frac{b}{2}H_2O + N_c$.

Compound.	Molecular formula.	Heat of combustion of the vapour at the boiling-point.	Heat of combustion of the gas at 18°.	Heat of formation of the products.	Heat of formation of the compound at constant pressure.	Heat of formation of the compound at constant volume.
		CYANOGEN.				
Cyanogen	C_2N_2	—	259,620 c	193,920 c	−65,700 c	−65,700 c
Hydrogen cyanide	HCN	158,710 c	158,620	131,140	−27,480	−27,480
		NITRILES.				
Acetonitrile	$CH_3 . CN$	313,200	312,140	296,460	−15,680	−16,260
Propionitrile	$C_2H_5 . CN$	473,320	471,450	461,780	− 9,670	−10,830
		AMINES.				
Ammonia	H_3N	—	90,650	102,540	+11,890	+11,310
Methylamine	$CH_3 . NH_2$	—	258,320	267,860	9,540	8,380
Dimethylamine	$(CH_3)_2 . NH$	—	420,460	433,180	12,720	10,980
Trimethylamine	$(CH_3)_3 . N$	—	582,630	598,500	15,870	13,550
Ethylamine	$C_2H_5 . NH_2$	415,690	415,670	433,180	17,510	15,770
Diethylamine	$(C_2H_5)_2 . NH$	735,780	734,500	763,820	29,320	26,420
Triethylamine	$(C_2H_5)_3 . N$	1,055,640	1,052,380	1,094,460	42,080	38,020
Propylamine	$C_3H_7 . NH_2$	576,620	575,740	598,500	22,760	20,420
Isobutylamine	$C_4H_9 . NH_2$	726,990	725,360	763,820	38,460	35,560
Amylamine	$C_5H_{11} . NH_2$	893,710	890,580	929,140	38,560	35,080
Allylamine	$C_3H_5 . NH_2$	532,080	531,280	530,140	− 1,140	− 2,880
Aniline	$C_6H_5 . NH_2$	844,240	838,470	821,020	−17,450	−19,190
Pyridine	C_5H_5N	677,920	675,070	655,700	−19,370	−20,530
Piperidine	$C_5H_{11}N$	837,120	833,790	860,780	+26,990	+24,090

TABLE 44.

NITROCOMPOUNDS, NITRITES, AND NITRATES.

Combustion : $C_aH_bNO_c + \left(2a + \frac{b}{2} - c\right)O = aCO_2 + \frac{b}{2}H_2O + N.$

Compound.	Molecular formula.	Heat of combustion		Heat of formation of the products.	Heat of formation of the compound	
		of the vapour at the boiling-point.	of the gas at 18°.		at constant pressure.	at constant volume.
Nitromethane	$CH_3 . NO_2$	182,230 c	180,900 c	199,500 c	18,600 c	17,440 c
Nitroethane	$C_2H_5 . NO_2$	340,040	337,940	364,820	26,880	25,140
Ethyl nitrite	$C_2H_5 . O . NO$	334,200	334,210	364,820	30,610	28,870
Isobutyl nitrite	$C_4H_9 . O . NO$	649,400	647,660	695,460	47,800	44,900
Amyl nitrite	$C_5H_{11} . O . NO$	815,860	812,640	860,780	48,140	44,600
Ethyl nitrate	$C_2H_5 . O . NO_2$	325,690	324,040	364,820	40,780	38,750

CHAPTER XIV

THEORETICAL INVESTIGATION OF THE THERMAL PHENOMENA OF VOLATILE ORGANIC SUBSTANCES, AND THEIR DEPENDENCE UPON THE MOLECULAR CONSTITUTION

THE preceding chapter contains the experimental results of my determinations of the heats of combustion of 120 organic compounds arranged in a tabular manner, as well as the thermal effect on formation of the compounds from their elements, these latter values being derived from the heats of combustion. In all the experiments it is assumed that the substance is present in the *state of gas or vapour* at 18°, that the combustion takes place at *constant pressure*, and also that the products are liquid water, gaseous carbon dioxide, sulphur dioxide, nitrogen, and chlorine; bromine and iodine as vapours at 18°.

From the molecular heat of combustion we can calculate the thermal effect on formation of the molecule from its elements, since this is the difference between the heat of formation of the products (such as water, carbon dioxide, sulphur dioxide, etc.) and the heat of combustion of the substance. *The heats of formation* have been given in the preceding tables both at constant pressure and at constant volume, and expressed in gram-calories; but in the tables which follow, the *kilogram-calorie* will be taken as unit.

The task now before us is to determine, if possible, to what extent the heat of combustion, and consequently also the heat of formation, is dependent upon the molecular constitution.

1. Identity of the Four Valencies of Carbon.

Carbon is the fundamental element in all the so-called organic compounds, and the tetravalence of the carbon atom mainly accounts for the large number of compounds formed. The first question which presents itself in a study of the dependence of the thermal phenomena upon the molecular constitution must therefore be to ascertain whether there is any difference between the four valencies of the carbon atom with respect to the strength with which the atom is able to combine with other atoms by means of one or other of its valencies.

In order to answer this question I measured the heats of combustion of methane, and of the four hydrocarbons derived therefrom by the successive replacement of the hydrogen atoms by means of the CH_3 group; that is, of ethane, propane, trimethylmethane, and tetramethylmethane. From Table 35 we find that

Hydrocarbon.	Molecular formula.	Heat of combustion.	Difference.
Methane	H_4C	211·93 Cal.	
Ethane	$H_3C \cdot CH_3$	370·44 ,,	1 × 158·51 Cal.
Propane	$H_2C \cdot (CH_3)_2$	529·21 ,,	2 × 158·64 ,,
Trimethylmethane .	$HC \cdot (CH_3)_3$	687·19 ,,	3 × 158·42 ,,
Tetramethylmethane .	$C(CH_3)_4$	847·11 ,,	4 × 158·79 ,,

The difference between the heats of combustion of these four derivatives of methane and of that of methane itself are to be found in the fourth column; from these numbers, which are seen to be multiples of a constant magnitude, it is evident that the replacement of each hydrogen atom in methane by a CH_3 group produces the same thermal effect; or in other words, that the *four valencies of carbon are identical.*

This fact excludes the possibility of there being two hydrocarbons of the formula C_2H_6; such as, for instance, dimethyl, $CH_3 \cdot CH_3$, and ethyl hydride, $H \cdot C_2H_5$; and it has been experimentally demonstrated that only one such hydrocarbon exists.

The heats of combustion of the two supposed compounds were found to be

Ethyl hydride	370·90 Cal. at	18·4°
Dimethyl	370·10 „	19·5°.

The first of these substances was formed by the decomposition of zinc ethyl by means of dilute hydrochloric acid, the second by electrolysis of sodium acetate (see *Therm. Unters.*, iv. 50). The two hydrocarbons are therefore identical, as are also the valencies of carbon.

Furthermore, investigation of the halogen compounds has proved that *isomeric chlorides have equal heats of combustion*, quite independently of which hydrogen atom in the hydrocarbon has been replaced by chlorine. Thus the heats of combustion of allyl chloride and of monochlorpropylene in the state of vapour at 18° (see Table 36) are

Allyl chloride	$CH_2 : CH . CH_2Cl$	454·68 Cal.
Monochlorpropylene. .	$CH_2 : CCl . CH_3$	453·37 „

The same holds good for ethylene chloride and ethylidene chloride, of which the heats of combustion are

Ethylene chloride . . .	$CH_2Cl . CH_2Cl$	296·36 Cal.
Ethylidene chloride. . .	$CH_3 . CHCl_2$	296·41 „

From the above-mentioned facts there can therefore be no doubt as to the *identity of the four valencies of the carbon atom.*

2. Heats of Combustion of Homologous Compounds.

The earlier researches on the heats of combustion of organic substances had already demonstrated the probability of the difference between the heats of combustion of two successive members in a series of homologous compounds being an approximately constant magnitude. My investigations help to throw further light on the validity of this assumption. The majority of the compounds investigated, of which the heats of combustion are given in the preceding tables, belong to 15 series of homologous compounds. If we represent the molecular formula of a member of such a series by M_a, and

consequently the first member by M_1, the formula will be the following :—

$$M_a = M_1 + (a - 1)CH_2,$$

and if we represent the heat of combustion of the term M_a by fM_a, this will be equal to

$$fM_a = fM_1 + (a - 1)D, \quad . \quad . \quad . \quad (1)$$

where D is the constant difference found between the heats of combustion of two successive members.

From the numbers contained in the tables we find that the following are the mean values of D for each group of compounds :—

Group.	Number of compounds investigated.	D
Paraffins	6	158·23 Cal.
Olefines	4	158·49 ,,
Acetylenes	2	157·50 ,,
Aromatic hydrocarbons . . .	3	159·72 ,,
Alcohols	5	158·86 ,,
Aldehydes and ketones	5	158·76 ,,
Esters	9	158·44 ,,
Eight groups	Mean value . .	158·57 ,,

Somewhat lower values for D were found in the following groups :—

Group.	Number of compounds investigated.	D
Halogen compounds	15	157·41 Cal.
Nitriles and amines	10	157·70 ,,
Acids	3	157·69 ,,
Ethers	3	155·58 ,,
Sulphides	4	157·22 ,,
Nitrocompounds	2	157·04 ,,
Seven groups	Mean value . .	157·11 ,,

So that of the total 120 compounds investigated 71 give values which are in agreement with the assumption already

mentioned; the remaining 49 compounds are isolated examples, and not successive members of homologous series.

Thus we see that the *difference between the heats of combustion of two neighbouring members in a series of homologous compounds is a constant which shows very small variations for the different series;* these, however, seem to arrange themselves into two main groups, the one with an average value of D equal to 158·57 Cal., the other with a value of 157·11 Cal. I shall refer to the possible reason of this difference later on when considering the results of the separate groups. If we assume the difference D to be a constant with respect to each series of homologous compounds, the heats of combustion of all the members will depend only upon two values for each group, namely, upon the heat of combustion of one member, and upon the value of D in accordance with equation (1).

3. Heat of Combustion of a Carbon Atom.

The carbon molecule as known to us in its various allotropic modifications, such as the diamond, graphite, amorphous carbon, etc., is a complex of atoms; but how many of these atoms there are in the molecule is quite unknown. When compounds of carbon are formed, containing one atom only of carbon in the molecule, such as CO, CO_2, CH_4, HCN, etc., the carbon molecule must of necessity be first split up into atoms, and this entails absorption of energy.

The formation of such a compound with one atom of carbon in the molecule will therefore take place with evolution of energy, and the magnitude of this will be equal to the difference between the amount of energy resulting from the affinity of the carbon atom for the other constituent of the compound, and that part of the energy set free from each one of its atoms which is consumed in the splitting up of the carbon molecule.

Thus if, for example, the heat of combustion of amorphous carbon is 96·96 Cal., this in no way represents the total energy which would be evolved in the union of a gram-molecule of oxygen with a gram-atom of carbon to form carbon dioxide, for the value would be diminished by that amount of energy

which was consumed in the breaking up of the carbon molecule. If we put the number of atoms in the carbon molecule as equal to n, and the amount of energy consumed by the dissociation of the molecule into separate atoms as equal to $n \times d$, then every atom of carbon occasions a consumption of energy equal to d.

Hence it follows that the heat evolved when 1 *gram-atom* of carbon unites with 1 gram-molecule of oxygen must be d times greater than that which is observed in the case of molecular carbon, *e.g.* 96·96 Cal. + d.

Furthermore, I have found that the thermal effect when 1 gram-molecule of oxygen unites with carbon to form 2 gram-molecules of carbon monoxide amounts to 58·58 Cal. at constant volume. In this case 2 gram-atoms of carbon must have been split off from the carbon molecule, and this would occasion a consumption of energy equal to $2d$, so that the thermal value of the formation of 2 gram-molecules of carbon monoxide from 1 gram-molecule of oxygen and 2 *gram-atoms* of carbon will be equal to 58·58 Cal. + 2 × d.

In each of these examples 1 gram-molecule of oxygen is decomposed; in the first case with the formation of the molecule $O : C : O$, in the second with that of two molecules of $O : C$ and $C : O$. In both instances the two oxygen atoms are each united to two out of the four valencies of carbon. Now, since the four valencies of carbon are identical, the heat evolved in the two cases must also be equal, and we therefore have—

$$96{\cdot}96 \text{ Cal.} + d = 58{\cdot}58 \text{ Cal.} + 2d,$$

whence it follows that—

$$d = 38{\cdot}38 \text{ Cal.}$$

That is to say, *when a molecule of solid carbon, such as is found in amorphous carbon, is to be dissociated into its atoms with the production of a condition of motion equal to that which it has as the constituent of a gaseous compound, the solid carbon must be supplied with an amount of energy equal to* 38·38 *Cal. for every gram-atom set free.* The carbon atom thus liberated will therefore, as the constituent of a gaseous compound, have a

heat of combustion which is 38·38 Cal. greater than that which corresponds to twelve parts by weight of amorphous carbon.

If now we represent the *absolute heat of combustion of a gram-atom of carbon* by x, we obtain

$$x = 96{\cdot}96 \text{ Cal.} + 38{\cdot}38 \text{ Cal.} = 135{\cdot}34 \text{ Cal.}$$

This value is naturally twice as great as the heat of combustion of 1 gram-molecule of carbon monoxide at constant volume, namely 67·67 Cal.; for carbon monoxide on combustion takes up 1 atom of oxygen, the carbon atom, on the other hand, requires 2 atoms of oxygen to form carbon dioxide.

It should be noted *that the value thus found for x is independent of the allotropic condition of the carbon*, whereas d has a special value for each allotropic modification. Thus for the diamond, when the heat of combustion is taken as about 94·00 Cal., the value for d is 41·34 Cal.

4. Dependence of the Heat of Combustion upon the Molecular Constitution—Thermochemical Constants.

(*a*) If we wish to establish some connection between the heat of combustion of a compound and its molecular constitution, it is as well to start with the hydrocarbons, since their molecules are composed only of two kinds of atoms, and one might therefore expect to find the simplest relations for their heats of combustion.

If we represent the molecule of the hydrocarbon by C_aH_{2b}, and also remember, as has been proved above, that the four valencies of the carbon atom are identical, we are justified in assuming that all the hydrogen atoms in the molecule are united to the carbon atom in the same manner, and that they must therefore all contribute equally to the heat of combustion of the molecule.

Suppose now we represent *that part of the heat of combustion which corresponds to each of the carbon atoms in the molecule by x, and that part of it due to each one of the hydrogen atoms*

united to the carbon by y, then the heat of combustion of the molecule must be

$$fC_aH_{2b} = ax + 2by - \Sigma v, \quad . \quad . \quad . \quad (3)$$

where Σv indicates the summation of the energy corresponding to the collective bonds between the carbon atoms. The energy due to this latter must therefore be overcome by the combustion, since the product of the reaction is carbon dioxide, which contains only a single atom of carbon in the molecule.

When the carbon atoms of a hydrocarbon are united only by *single* bonds, then their number will be $2a - b$. And representing the thermal effect due to the so-called single bond by v_1, the equation given above becomes

$$fC_aH_{2b} = ax + 2by - (2a - b)v_1,$$

which may finally be put in the following more convenient form :—

$$fC_aH_{2b} = a(x - 2v_1) + b(2y + v_1) = aA + bB \quad (4)$$

The heat of combustion will therefore be dependent upon the two constants A and B, the magnitudes of which can be derived from the values found experimentally for the heats of combustion of two members in a homologous series of hydrocarbons, since, as has already been explained, we may assume that there is a constant difference between the heats of combustion of two successive members in a homologous series. Now, since the difference in composition between two such members is CH_2, the difference in the heat of combustion will be

$$D = A + B = x + 2y - v_1 \quad . \quad . \quad . \quad (5)$$

When the hydrocarbon contains *double* bonds, p_2, and when the energy due to these bonds is p_2v_2, then the number of single bonds will not be $2a - b$, but $2p_2$ less than this; Σv will therefore be $2p_2v_1$ lower and p_2v_2 greater than it would be in accordance with equation (4); the heat of combustion will thus be

$$fC_aH_{2b} = aA + bB + p_2(2v_1 - v_2) \quad . \quad . \quad (6)$$

If the hydrocarbon also contains *triple* bonds, p_3, the heat

of combustion will for the same reason be increased by $p_3(3v_1 - v_3)$, and will consequently be

$$fC_aH_{2b} = aA + bB + p_2(2v_1 - v_2) + p_3(3v_1 - v_3) \quad (7)$$

This, therefore, is the general equation for calculating the heat of combustion of a hydrocarbon. In this expression there are four constants; the first two of these can be derived from the heats of combustion of the paraffins, the other two from those of the non-saturated hydrocarbons.

Now, since 1 gram-molecule of C_aH_{2b} requires $\left(a + \frac{b}{2}\right)$ gram-molecules of oxygen for complete combustion, and forms a gram-molecules only of the gaseous product (carbon dioxide), the combustion must therefore be attended by a diminution in volume corresponding to $\left(1 + \frac{b}{2}\right)$ molecular volumes. By this means the heat evolved is increased by $\left(1 + \frac{b}{2}\right)0{\cdot}58$ Cal., which must of course be subtracted from the experimental result in order to obtain a value independent of external conditions; that is to say, the heat of combustion at *constant volume*.

If now from the heats of combustion at constant volume (see Table 45) of the first five members of the *paraffin* series we calculate the probable values of A and B by means of the method of least squares, we arrive at the following result:—

$$\begin{aligned} A &= 105{\cdot}92 \text{ Cal.} = (x - 2v_1) \\ B &= 52{\cdot}42 \quad \text{,,} \quad = (2y + v_1) \end{aligned} \quad \cdot \cdot \quad (8)$$

In the same way from the heats of combustion at constant volume of the four hydrocarbons, C_2H_4, C_3H_6, C_4H_8, and C_6H_{10} (diallyl), which together contain five *double* bonds, we can find the value of $(2v_1 - v_2)$. For since the sum of the heats of combustion of these four hydrocarbons is 2403·15 Cal., we have the following equation, in which A and B have the values given in (8):—

$$\begin{aligned} 15A + 14B + 5(2v_1 - v_2) &= 2403{\cdot}45 \text{ Cal.} \\ 2322{\cdot}40 \text{ Cal.} + 5(2v_1 - v_2) &= 2403{\cdot}15 \text{ ,,} \end{aligned}$$

whence it follows that—

$$(2v_1 - v_2) = 16{\cdot}15 \text{ Cal.} \quad . \quad . \quad . \quad . \quad (9)$$

For the calculation of the fourth constant $(3v_1 - v_3)$, we make use of the heats of combustion of the three hydrocarbons, C_2H_2, C_3H_4, C_6H_6 (dipropargyl), which together contain four triple bonds, and of which the sum of the heats of combustion amounts to 1657·00 Cal. at constant volume. We thus have

$$11A + 6B + 4(3v_1 - v_3) = 1657{\cdot}00 \text{ Cal.}$$
$$1479{\cdot}52 \text{ cal.} + 4(3v_1 - v_3) = 1657{\cdot}00 \quad ,,$$

and from this we find that—

$$(3v_1 - v_3) = 44{\cdot}37 \text{ Cal.} \quad . \quad . \quad . \quad (10)$$

In this manner we have determined the values of the four constants which enter into equation (7), and can therefore calculate the heats of combustion of the members of three series of hydrocarbons. The agreement between the values calculated by means of these constants and those found experimentally are shown in the table on p. 392.

The four constants thus found can now be utilized in an endeavour to determine the values of x, y, v_1, v_2, and v_3, which were found only by implication in the preceding determination.

(*b*) In equation (8) x, or the heat of combustion of the carbon atom of a gaseous hydrocarbon, is expressed as dependent upon v_1; now, since equations (9) and (10) give the relation between v_1, v_2, and v_3, x can also be represented in terms of v_2 and v_3, and we then have the following three values:—

$$\left.\begin{aligned} x &= 105{\cdot}92 \text{ Cal.} + 2v_1 \\ x &= 122{\cdot}07 \quad ,, \quad + v_2 \\ x &= 135{\cdot}50 \quad ,, \quad + \tfrac{2}{3}v_3 \end{aligned}\right\} \quad . \quad . \quad . \quad (11)$$

From this comparison, and also from equations (9) and (10), it is evident that the so-called double bond corresponds to a smaller thermal effect than two single bonds, and similarly that the triple bond has a far smaller effect than three single bonds.

If the carbon molecule is saturated with respect to the linkages between its constituent atoms, the molecule must contain

of combustion will for the same reason be increased by $p_3(3v_1 - v_3)$, and will consequently be

$$fC_aH_{2b} = aA + bB + p_2(2v_1 - v_2) + p_3(3v_1 - v_3) \quad (7)$$

This, therefore, is the general equation for calculating the heat of combustion of a hydrocarbon. In this expression there are four constants; the first two of these can be derived from the heats of combustion of the paraffins, the other two from those of the non-saturated hydrocarbons.

Now, since 1 gram-molecule of C_aH_{2b} requires $\left(a + \frac{b}{2}\right)$ gram-molecules of oxygen for complete combustion, and forms a gram-molecules only of the gaseous product (carbon dioxide), the combustion must therefore be attended by a diminution in volume corresponding to $\left(1 + \frac{b}{2}\right)$ molecular volumes. By this means the heat evolved is increased by $\left(1 + \frac{b}{2}\right)0{\cdot}58$ Cal., which must of course be subtracted from the experimental result in order to obtain a value independent of external conditions; that is to say, the heat of combustion at *constant volume*.

If now from the heats of combustion at constant volume (see Table 45) of the first five members of the *paraffin* series we calculate the probable values of A and B by means of the method of least squares, we arrive at the following result:—

$$\begin{aligned} A &= 105{\cdot}92 \text{ Cal.} = (x - 2v_1) \\ B &= 52{\cdot}42 \quad \text{,,} \quad = (2y + v_1) \end{aligned} \quad \cdots \quad (8)$$

In the same way from the heats of combustion at constant volume of the four hydrocarbons, C_2H_4, C_3H_6, C_4H_8, and C_6H_{10} (diallyl), which together contain five *double* bonds, we can find the value of $(2v_1 - v_2)$. For since the sum of the heats of combustion of these four hydrocarbons is 2403·15 Cal., we have the following equation, in which A and B have the values given in (8):—

$$\begin{aligned} 15A + 14B + 5(2v_1 - v_2) &= 2403{\cdot}45 \text{ Cal.} \\ 2322{\cdot}40 \text{ Cal.} + 5(2v_1 - v_2) &= 2403{\cdot}15 \text{ ,,} \end{aligned}$$

whence it follows that—

$$(2v_1 - v_2) = 16{\cdot}15 \text{ Cal.} \quad . \quad . \quad . \quad . \quad (9)$$

For the calculation of the fourth constant $(3v_1 - v_3)$, we make use of the heats of combustion of the three hydrocarbons, C_2H_2, C_3H_4, C_6H_6 (dipropargyl), which together contain four triple bonds, and of which the sum of the heats of combustion amounts to 1657·00 Cal. at constant volume. We thus have

$$11A + 6B + 4(3v_1 - v_3) = 1657{\cdot}00 \text{ Cal.}$$
$$1479{\cdot}52 \text{ cal.} + 4(3v_1 - v_3) = 1657{\cdot}00 \text{ ,,}$$

and from this we find that—

$$(3v_1 - v_3) = 44{\cdot}37 \text{ Cal.} \quad . \quad . \quad . \quad (10)$$

In this manner we have determined the values of the four constants which enter into equation (7), and can therefore calculate the heats of combustion of the members of three series of hydrocarbons. The agreement between the values calculated by means of these constants and those found experimentally are shown in the table on p. 392.

The four constants thus found can now be utilized in an endeavour to determine the values of x, y, v_1, v_2, and v_3, which were found only by implication in the preceding determination.

(*b*) In equation (8) x, or the heat of combustion of the carbon atom of a gaseous hydrocarbon, is expressed as dependent upon v_1; now, since equations (9) and (10) give the relation between v_1, v_2, and v_3, x can also be represented in terms of v_2 and v_3, and we then have the following three values:—

$$\left.\begin{aligned} x &= 105{\cdot}92 \text{ Cal.} + 2v_1 \\ x &= 122{\cdot}07 \text{ ,,} + v_2 \\ x &= 135{\cdot}50 \text{ ,,} + \tfrac{2}{3}v_3 \end{aligned}\right\} \quad . \quad . \quad . \quad (11)$$

From this comparison, and also from equations (9) and (10), it is evident that the so-called double bond corresponds to a smaller thermal effect than two single bonds, and similarly that the triple bond has a far smaller effect than three single bonds.

If the carbon molecule is saturated with respect to the linkages between its constituent atoms, the molecule must contain

that is to say, that part of the heat of combustion of the molecule which is due to each atom of hydrogen united to the atom of carbon. We thus have—

$$B = 2y + v_1 = 52{\cdot}40 \text{ Cal.} \qquad v_1 = 14{\cdot}71 \text{ Cal.},$$

whence it follows that—

$$2y = 37{\cdot}69 \text{ Cal.} \quad . \quad . \quad . \quad . \quad . \quad (14)$$

A comparison of this value with the heat of combustion of 1 gram-molecule of hydrogen brings us finally to a determination of the thermal effect corresponding to the bond between an atom of hydrogen and an atom of carbon. In calculating the heat of combustion of a hydrocarbon, the products of the combustion are assumed to be gaseous carbon dioxide and liquid water. The thermal value on formation of 1 gram-molecule of water at constant pressure is shown by my researches (p. 193) to be 68·36 Cal. If now we subtract from this value $\frac{3}{2} \times 0{\cdot}58$ Cal., we obtain 67·49 Cal. as the *heat of combustion of* 1 *gram-molecule of hydrogen at constant volume.*

This value can, however, not be compared directly with the heat of combustion of 37·69 Cal. found above for 2 gram-atoms of hydrogen united to the carbon; for the first value corresponds to the combustion of a *gram-molecule* of hydrogen, the last to the combustion of two *gram-atoms*. If we represent the thermal value of the union of two atoms of hydrogen to a molecule by $h \,.\, h$, then the heat of combustion of 2 gram-atoms of hydrogen will be 67·49 Cal. $+ h \,.\, h$, which on subtraction of 37·69 Cal. gives 29·80 Cal. $+ h \,.\, h$ as the thermal value due to the union of 2 gram-atoms of hydrogen to a carbon gram-atom. Representing this value by $2c \,.\, h$, we have—

$$2c \,.\, h = 29{\cdot}80 \text{ Cal.} + h \,.\, h,$$

and therefore the thermal effect when 1 gram-molecule of hydrogen gives up its two gram-atoms to enter into combination with a gram-atom of carbon will be

$$2r = 2c \,.\, h - h \,.\, h = 29{\cdot}80 \text{ Cal.} \quad . \quad . \quad (15)$$

(*d*) The preceding investigations have resulted in the

following values for *the constants which enter into the heat of combustion of the hydrocarbons at constant volume :—*

1. The heat of combustion of each carbon gram-atom in a gas or in the vapour of a compound amounts to

$$x = 135{\cdot}34 \text{ Cal.}$$

2. The heat of combustion of every two hydrogen gram-atoms united to a carbon gram-atom amounts to

$$2y = 37{\cdot}69 \text{ Cal.}$$

3. The thermal value corresponding to the different kinds of linkages between two gram-atoms of carbon is for the hydrocarbons

$$v_1 = 14{\cdot}71 \text{ Cal.} \qquad v_2 = 13{\cdot}27 \text{ Cal.} \qquad v_3 = 0.$$

4. The thermal effect due to the bond between hydrogen and a carbon atom amounts, for each gram-molecule of hydrogen of which the two gram-atoms enter into combination, to

$$2r = 29{\cdot}80 \text{ Cal.} = 2c.h - h.h.$$

5. For the splitting up of the carbon molecule into separate gaseous atoms, each twelve parts by weight of carbon requires an amount of heat equal to the difference between x—that is to say, 135·34 Cal.—and the heat of combustion of the carbon. In the case of amorphous carbon, of which the heat of combustion is 96·96 Cal., the difference for each gram-atom of carbon is

$$d = 38{\cdot}38 \text{ Cal.}$$

6. The difference between the heats of combustion of two successive members in a homologous series of hydrocarbons is

$$x + 2y - v_1 = 158{\cdot}32 \text{ Cal.}$$

We shall now endeavour to determine how far the fundamental values given above can serve for the interpretation of

the values of the heats of combustion and of formation of the different series of volatile organic compounds.

5. Heats of Combustion of the Hydrocarbons.

The heats of combustion of the hydrocarbons are to be found from the general equation (7)—

$$f\mathrm{C_aH_{2b}} = aA + bB + p_2(2v_1 - v_2) + p_3(3v_1 - v_3),$$

in which p_2 and p_3 represent the number of double and triple bonds; the constants A and B are 105·92 and 52·40 Cal., and $(2v_1 - v_2)$ and $(3v_1 - v_3)$ have values of 16·15 and 44·13 Cal. We can also make use of the simpler equation (3)—

$$f\mathrm{C_aH_{2b}} = ax + 2by - \Sigma v,$$

since we can substitute 135·34 and 37·69 Cal. for x and $2y$, and calculate Σv from the values given above for the different linkages, namely 14·71 Cal., 13·27 Cal., and zero.

TABLE 45.

HEATS OF COMBUSTION OF THE HYDROCARBONS.

Compound.	C_aH_{2b}	Heat of combustion at constant volume.		
		Experimental.	Calculated.	Difference.
		Cal.	Cal.	Cal.
Methane	CH_4	210·77	210·72	+0·05
Ethane	C_2H_6	368·99	369·04	−0·05
Propane	C_3H_8	527·47	527·36	+0·11
Trimethylmethane . .	C_4H_{10}	685·16	685·68	−0·52
Tetramethylmethane .	C_5H_{12}	844·79	844·00	+0·79
Ethylene	C_2H_4	332·19	332·79	−0·60
Propylene	C_3H_6	491·29	491·11	+0·18
Isobutylene	C_4H_8	648·88	649·43	−0·55
Diallyl.	C_6H_{10}	930·79	929·82	+0·97
Acetylene	C_2H_2	309·18	308·37	+0·81
Allylene	C_3H_4	466·39	466·69	−0·30
Dipropargyl	C_6H_6	881·43	880·98	+0·45

In the preceding table the heats of combustion of the

hydrocarbons calculated in this manner are compared with the experimental results, these latter values being reduced to constant volume by subtracting $\left(1 + \frac{b}{2}\right) 0{\cdot}58$ Cal. from the heat of combustion at constant pressure of C_aH_{2b}, since the constants given above are only valid at constant volume. All the values are expressed in kilogram-calories, corresponding to 1000 c.

The agreement between the calculated heats of combustion and those found experimentally is therefore in the highest degree satisfactory; in one case only does the difference amount to $\frac{1}{4}$ per cent. of the heat of combustion, which shows that the calculated values for the constants must be very nearly correct. To what extent they also hold good in the case of the aromatic compounds will be shown in the following pages.

6. Constitution of Benzene.

The constitution of benzene has been a much-disputed problem; for, on the one hand, it was assumed that the six carbon atoms were united by three single and by three double bonds, on the other, that the molecule contained nine single bonds. The investigations described have confirmed the accuracy of the last supposition. A comparison between the heats of combustion of the phenyl and the ethyl compounds will serve to illustrate this point.

Now, as the molecules of the phenyl and of the corresponding ethyl compounds contain respectively six and two atoms of carbon in the radical, but are, for the rest, composed of the same elements, therefore the differences in their heats of combustion will be dependent only upon the different number of carbon atoms, and upon the consequent difference in the number of linkages between the carbon atoms of the radical. Hence the difference in the heats of combustion will be the same, whether we make use of the results of direct experiment, or else first reduce these to the corresponding values at

constant volume. The experimental results at constant pressure were as follows :—

Compound.	Heat of combustion.	Difference.
C_6H_6	799·35 Cal.	428·91 Cal.
C_2H_6	370·44 „	
$C_6H_5.OH$	768·76 „	428·23 „
$C_2H_5.OH$	340·53 „	
$C_6H_5.O.CH_3$	936·30 „	430·43 „
$C_2H_5.O.CH_3$	505·87 „	
C_6H_5Cl	763·88 „	429·77 „
C_2H_5Cl	334·11 „	

The mean value of these four determinations is 429·33 Cal. Now, since the heats of combustion of, for example, the two hydrocarbons are given by

$$fC_6H_6 = 6x + 6y - \Sigma u$$
$$fC_2H_6 = 2x + 6y - v_1.$$

the difference will be

$$4x + v_1 - \Sigma u = 429{\cdot}33 \text{ Cal.}$$

If now for x and v_1 we insert the values given above, namely 135·34 and 14·71 Cal., respectively, we obtain—

$$\Sigma v = 126{\cdot}74 \text{ Cal.}$$

Now, if the benzene molecule contains three single and three double bonds, the value of Σv should be 83·94 Cal.; if, on the other hand, it contains nine single bonds of equal value, as in the other hydrocarbons, Σv should be equal to 132·39 Cal. There can therefore be no doubt but that the phenyl radical contains nine bonds, and the magnitude of the thermal effect corresponding to the single bonds will thus be 14·08 Cal., a value which differs very little from that found for the remainder of the hydrocarbons (14·71 Cal.).

Precisely the same result is obtained on comparing another phenyl compound, namely *aniline*, with *allylamine* (the reason that we cannot compare it with ethylamine will be referred to later). We thus have—

$fC_6H_5.NH_2 = 838{\cdot}47$ Cal.	307·19 Cal.
$fC_3H_5.NH_2 = 531{\cdot}28$ „	

Since the allyl radical contains a single and a double bond, this difference of 307·19 Cal. must, in accordance with what has been stated above, correspond to

$$3x + v_1 + v_2 - \Sigma u = 307{\cdot}19 \text{ Cal.},$$

which, on substitution of the known constants, gives

$$\Sigma u = 126{\cdot}81 \text{ Cal.},$$

and is thus in complete agreement with the values derived from the other four phenyl compounds. Consequently each of the nine bonds between the carbon atoms of benzene corresponds to a thermal effect of

$$u = 14{\cdot}09 \text{ Cal.}$$

Thus the carbon atoms of the phenyl radical are less strongly bound (0·62 Cal.) than is the case with the chain hydrocarbons; but an explanation of this behaviour readily suggests itself. It is quite reasonable to assume that the distance apart and relative positions of the carbon atoms in the molecule are not the same in the different series of compounds, so that the strength with which the atoms are bound together will also vary.

The constants for the heats of combustion of the aromatic hydrocarbons will therefore show slight deviations from those of the remaining hydrocarbons, namely—

$A' = (x - 2u) = 107{\cdot}16$ Cal.
$B' = (2y + u) = 51{\cdot}78$ „ } Aromatic hydrocarbons.

From these constants we can now calculate the heats of combustion of the aromatic hydrocarbons. The table below contains a comparison of these values with the experimental results, calculated at constant volume.

TABLE 46.

AROMATIC HYDROCARBONS.

Hydrocarbon.	C_nH_{2b}	Heat of combustion at constant volume.		
		Experimental.	Calculated.	Difference.
Benzene	C_6H_6	797·90 Cal.	798·30 Cal.	−0·40 Cal.
Toluene	C_7H_8	953·94	957·24	−3·30
Mesitylene	C_9H_{12}	1279·99	1275·12	+4·37
Pseudocumene . . .	C_9H_{12}	1279·19		

The differences in the experimental and calculated values for the higher members amount only to $\frac{1}{3}$ per cent. of the heats of combustion.

7. Heats of Formation of the Hydrocarbons.

The heat of formation of a compound is the difference between the heats of combustion of the constituents and that of the compound itself. Thus the heat of formation of a hydrocarbon, C_aH_{2b}, will be

$$(C_a, H_{2b}) = a(C, O_2) + b(H_2, O) - fC_aH_{2b}.$$

The heat of formation of 1 gram-molecule of water at constant pressure is 68·36 Cal., at *constant volume* it is 67·49 Cal., and we have found above that the heat of combustion of a gram-atom of carbon in a gaseous compound amounts to 135·34 Cal. The heat of formation at constant volume will therefore be

$$(C_a, H_{2b}) = a \times 135{\cdot}34 \text{ Cal.} + b \times 67{\cdot}49 \text{ Cal.} - fC_aH_{2b} \quad (17)$$

The magnitude 135·34 Cal. is, as already described, independent of the allotropic state of the carbon.

We shall call the thermal value calculated by means of (17) the *absolute heat of formation* of the compound, and represent it by P. It is easy to calculate this value by adding on $a \times 38{\cdot}38$ Cal. to the heats of formation given in column 7 of Tables 35 to 44; for the values there given are derived from the heat of combustion of amorphous carbon (96·96 Cal.), and this is 38·38 Cal. lower than the absolute heat of combustion of 1 gram-atom of carbon in a gaseous compound.

It is evident from what has been stated above that the *absolute heat of formation* of a compound is equal to the *sum of the thermal values corresponding to the collective linkages between the atoms of the molecule.* The following table contains the heats of formation of the hydrocarbons, the total number of linkages in the molecule, and the measure of the heat of formation due to each individual bond in the molecule; r and v represent the values of the bonds between a carbon atom and either an atom (half-molecule) of hydrogen or another carbon atom.

Molecule.	P Heat of formation.	n Number of bonds.	$P = nQ$
CH_4	59·55 Cal.	$4r$	$4 \times 14{\cdot}89$ Cal.
C_2H_6	104·16	$6r + v_1$	$7 \times 14{\cdot}88$
C_3H_8	148·51	$8r + 2v_1$	$10 \times 14{\cdot}85$
C_4H_{10}	193·65	$10r + 3v_1$	$13 \times 14{\cdot}90$
C_5H_{12}	236·85	$12r + 4v_1$	$16 \times 14{\cdot}80$
Sum . .	742·72 Cal.	$40r + 10v_1$	$50 \times 14{\cdot}85$ Cal.
C_2H_4	73·47 Cal.	$4r + v_2$	$5 \times 14{\cdot}69$ Cal.
C_3H_6	117·20	$6r + v_2 + v_1$	$8 \times 14{\cdot}65$
C_4H_8	162·44	$8r + v_2 + 2v_1$	$11 \times 14{\cdot}77$
C_5H_{10}	208·55	$10r + v_2 + 3v_1$	$14 \times 14{\cdot}90$
C_6H_{10}	218·70	$10r + 2v_2 + 3v_1$	$15 \times 14{\cdot}58$
Sum . .	780·36 Cal.	$38r + 6v_2 + 9v_1$	$53 \times 14{\cdot}74$ Cal.
C_2H_2	28·99 Cal.	$2r + v_3$	$2 \times 14{\cdot}49$ Cal.
C_3H_4	74·61	$4r + v_3 + v_1$	$5 \times 14{\cdot}92$
C_6H_6	133·08	$6r + 2v_3 + 3v_1$	$9 \times 14{\cdot}79$
Sum . .	236·68 Cal.	$12r + 4v_3 + 4v_1$	$16 \times 14{\cdot}79$ Cal.

We have already shown that v_3 is equal to zero, and has therefore no influence on the heat of formation of the molecule. The very marked agreement in magnitude of the constant Q in the three series of hydrocarbons suggests that the heat of formation follows the simple law, $P = nQ$, and is consequently proportional to the number of bonds. This is, however, not correct, but we may justly conclude that there is very little difference between the magnitudes of r, v_1, and v_2; and this, indeed, has been proved to be the case above (see p. 391), where the values in question were found to be 14·90, 14·71, and 13·27 Cal. Hence it also follows that the agreement must be greatest in the paraffin series, and that the constant Q must have a slightly lower value in the olefine series, into the heats of formation of which the somewhat lower value of 13·27 Cal. for each of the double bonds enters. That *this ostensible accordance is only accidental* is apparent from the heat of formation of benzene, namely 216·6 Cal.; for since the number of bonds is $6r + 9v$, this value should, from the preceding remarks,

be equal to $15Q$; but Q would then be only 14·44 Cal., instead of about 14·80 Cal. as found above. This lack of agreement must necessarily be due to the bonds, v, in the benzene molecule having a lower value than those of the paraffins, namely 14·09 as against 14·71 Cal. (see p. 395).

A chance agreement similar to the above might prove very misleading in an investigation of the dependence of thermal effect upon the configuration of the molecule, as we might be tempted to draw quite unwarranted conclusions therefrom. The preceding example should therefore serve as a warning against premature generalization.

The heat of formation of a compound must, from what has been said above, be expressed as a function of certain constants. In the case of the hydrocarbons we have found that the thermal value on formation of a hydrocarbon, C_aH_{2b}, from hydrogen and atomic carbon is

$$(C_a, H_{2b}) = 2b \cdot r + \Sigma v \quad . \quad . \quad . \quad (18)$$

where $2r$ represents the amount of heat liberated when the two atoms of a hydrogen molecule combine with a carbon atom in a gaseous compound, and Σv is the thermal effect corresponding to the linkage between the carbon atoms. The magnitude of these constants in the case of the *aliphatic* hydrocarbons is as follows:—

$2r = 29{\cdot}80$ Cal. $\quad v_1 = 14{\cdot}71$ Cal. $\quad v_2 = 13{\cdot}27$ Cal. $\quad v_3 = 0$,

whilst the nine bonds between the carbon atoms in the phenyl radical amount only to

$$9u = 9 \times 14{\cdot}09 \text{ Cal.}$$

In the table below the calculated values for the absolute heats of formation of the hydrocarbons are compared with the experimental results.

TABLE 47.

ABSOLUTE HEATS OF FORMATION OF THE HYDROCARBONS.

Hydrocarbon.	Number of bonds.	Heat of formation, P, at constant volume.		
		Experimental.	Calculated.	Difference.
CH_4	$4r$	59·55 Cal.	59·60 Cal.	−0·05 Cal.
C_2H_6	$6r + v_1$	104·16 ,,	104·11 ,,	+0·05 ,,
C_3H_8	$8r + 2v_1$	148·51 ,,	148·62 ,,	−0·11 ,,
C_4H_{10}	$10r + 3v_1$	193·65 ,,	193·13 ,,	+0·52 ,,
C_5H_{12}	$12r + 4v_1$	236·88 ,,	237·64 ,,	−0·76 ,,
C_2H_4	$4r + v_2$	73·47 ,,	72·87 ,,	+0·60 ,,
C_3H_6	$6r + v_2 + v_1$	117·20 ,,	117·38 ,,	−0·18 ,,
C_4H_8	$8r + v_2 + 2v_1$	162·44 ,,	161·89 ,,	+0·55 ,,
C_5H_{10}	$10r + v_2 + 3v_1$	208·55 ,,	206·45 ,,	+2·10 ,,
C_6H_{10}	$10r + 2v_2 + 3v_1$	218·70 ,,	219·67 ,,	−0·97 ,,
C_2H_2	$2r + v_3$	28·99 ,,	29·80 ,,	−0·81 ,,
C_3H_4	$4r + v_3 + v_1$	74·61 ,,	74·31 ,,	+0·30 ,,
C_6H_6	$6r + 2v_3 + 3v_1$	133·08 ,,	133·53 ,,	−0·45 ,,
C_6H_6	$6r + 9u$	216·61 ,,	216·21 ,,	+0·40 ,,
C_7H_8	$8r + 9u + v_1$	263·40 ,,	260·72 ,,	+2·68 ,,

The agreement is therefore, on the whole, very satisfactory.

8. Alcohols.

Twelve alcohols in all were investigated, and their absolute heats of formation, P, are given in the table below. The values were calculated in the usual manner, namely, by adding 38·38 Cal. to the numbers contained in the seventh column of Table 38 for each gram-atom of carbon. A comparison of these figures with the heats of formation of the corresponding hydrocarbons shows that in the case of the primary monohydric alcohols there is an almost constant difference; for the first three alcohols this difference equals 29·77 Cal., whilst the mean value for all seven alcohols is 28·92 Cal. It is thus evident that the constants entering into the heats of formation of the alcohols have approximately the same values as those in the case of the hydrocarbons; therefore here also we can put

$r = 14{\cdot}90$ Cal. $\quad v_1 = 14{\cdot}71$ Cal. $\quad v_2 = 13{\cdot}27$ Cal. $\quad v_3 = 0$.

The alcohol molecule contains a hydroxyl group, OH, united to a carbon atom, and has the general formula

$$C_aH_{2b-1}.OH.$$

The thermal effect, s, which corresponds to the formation of the group COH, can therefore be determined by subtracting from the heat of formation, P, of the alcohol, the thermal value corresponding to the remaining linkages in the molecule; that is to say, by putting

$$P - (2b - 1)r - \Sigma v = s \quad . \quad . \quad . \quad (19)$$

TABLE 48.

HEATS OF FORMATION OF THE ALCOHOLS.

Alcohol.	$C_aH_{2b-1}OH$	Heat of formation, P, at constant volume.	$(2b-1)r + \Sigma v$	s
		Cal.	Cal.	Cal.
Methyl alcohol .	$CH_3.OH$	88·96	44·70	44·26
Ethyl ,, .	$C_2H_5.OH$	133·78	89·21	44·57
Propyl ,, .	$C_3H_7.OH$	178·80	133·72	45·08
Isobutyl ,, .	$C_4H_9.OH$	222·06	178·23	43·83
Isoamyl ,, .	$C_5H_{11}.OH$	263·60	222·74	40·86
Allyl ,, .	$C_3H_5.OH$	144·89	102·48	42·41
Phenol	$C_6H_5.OH$	246·91	201·31	45·60
Isopropyl alcohol .	$C_3H_7.OH$	184·11	133·72	50·39
Dimethylethyl carbinol .	$C_5H_{11}.OH$	273·22	222·84	50·38
Propargyl alcohol .	$C_3H_3.OH$	110·77	59·41	51·36
Ethylene glycol .	$C_2H_4.(OH)_2$	175·91	74·31	2 × 50·80
Trimethyl carbinol	$C_4H_9.OH$	239·21	178·23	60·98

The value of s given in the preceding table is of approximately equal magnitude for the first seven alcohols, the average value being 43·80 Cal.; but for two of these, namely, allyl alcohol and isoamyl alcohol, the deviation from the mean value is rather great. If, however, we omit these two alcohols, the mean value for the remaining five will be 44·67 Cal., and this will be the thermal effect corresponding to the formation of the COH group of the primary alcohols.

On the other hand, the thermal effect corresponding to the COH group has a higher value for the following five alcohols. From this it is evident that the heat of formation of the primary alcohols is less than that of their secondary or tertiary isomers, as shown in the table below.

		Heats of formation.	Difference.
$C_3H_7.OH$	Propyl alcohol . . .	178·80 Cal.	5·30 Cal.
	Isopropyl alcohol . .	184·11 „	
$C_4H_9.OH$	Isobutyl alcohol . . .	222·06 „	17·15 „
	Trimethyl carbinol . .	239·21 „	
$C_5H_{11}.OH$	Isoamyl alcohol . . .	263·60 „	9·62 „
	Dimethylethyl carbinol .	273·22 „	

The value on formation of the COH group in the secondary and tertiary alcohols is 50·37 and 60·98 Cal. respectively.

Propargyl alcohol and ethylene glycol resemble the first series of alcohols, the heat of formation of each COH group in ethylene glycol being 50·80 Cal.; trimethyl carbinol has the highest value, namely 60·98 Cal. Possibly the more or less central position of the COH group in the molecule has some influence in this respect; thus for propyl and isopropyl alcohol, and trimethyl carbonyl, the grouping is

$$C.COH \qquad C.\overset{OH}{C}.C \qquad C.\overset{OH}{\overset{C}{C}}.C,$$

and the thermal values corresponding to these are

45·08 50·39 60·98 Cal.

It is noteworthy that the primary propargyl alcohol more closely resembles the secondary alcohols, whilst phenol, with respect to its COH group, is in complete agreement with the primary alcohols. Furthermore, it is to be noted that the differences in the heats of formation of propyl, allyl, and propargyl alcohol are equal to each other, namely—

			Difference.
Propyl alcohol . . .	$C_3H_7.OH$	178·80 Cal.	33·91 Cal.
Allyl alcohol	$C_3H_5.OH$	144·89 „	
Propargyl alcohol . .	$C_3H_3.OH$	110·77 „	34·12 „

In each of these cases there is a difference of two atoms of hydrogen in the molecule, but the bonds between the carbon atoms are not the same. At present there is no satisfactory explanation of these facts.

9. Aldehydes, Ketones, Acids, and Acid Anhydrides.

Tables 39 and 40 contain the heats of combustion of these substances at constant pressure, and in the seventh column are given the heats of formation at constant volume, starting from amorphous carbon. From the last value we can, in the usual manner, find the absolute heat of formation, P, of the compound by the addition of $a \times 38{\cdot}38$ Cal., where a is the number of carbon atoms in the molecule. These numbers will be found below in Table 49, where, in the last column, are also given the calculated values that the heats of formation of the groups COH, CO, COOH, and $(CO)_2O$ exercise on the heats of formation of the compounds. The constants r and v_1 are of the same magnitude as in the case of the hydrocarbons and alcohols, namely, $r = 14{\cdot}90$ Cal. and $v_1 = 14{\cdot}71$ Cal.

TABLE 49.

ALDEHYDES, KETONES, ACIDS, AND ACID ANHYDRIDES.

Substance.	Molecular formula.	Heat of formation, P, at constant volume.	Bonds $mr + nv_1$	$P - (mr + nv_1)$
		Cal.		Cal.
Acetic aldehyde	$CH_3 . COH$	124·63	$3r + v_1$	COH = 65·22
Propionic aldehyde	$C_2H_5 . COH$	168·93	$5r + 2v_1$	= 65·01
Isobutyric aldehyde	$C_3H_7 . COH$	212·83	$7r + 3v_1$	= 64·40
Dimethyl ketone	$CH_3 . CO . CH_3$	172·40	$6r + 2v_1$	CO = 53·58
Methylpropyl ketone	$CH_3 . CO . C_3H_7$	261·30	$10r + 4v_1$	= 53·46
Formic acid	$H . COOH$	133·73	r	COOH = 118·83
Acetic acid	$CH_3 . COOH$	180·89	$3r + v_1$	= 121·48
Propionic acid	$C_2H_5 . COOH$	222·85	$5r + 2v_1$	= 118·93
Acetic anhydride	$(C_2H_3O)_2O$	284·34	$6r + 2v_1$	$O\overset{CO}{\underset{CO}{}}$ = 165·52

(*a*) *Aldehydes and primary alcohols.*—A comparison of the heats of formation of the three aldehydes investigated with those of the corresponding alcohols shows that the aldehydes have a lower value than the alcohols. The values for P are as follows:—

Radical.	Alcohol.	Aldehyde.	Difference.
Ethyl	133·78 Cal.	124·63 Cal.	9·15 Cal.
Propyl. . . .	178·80 ,,	168·93 ,,	9·87 ,,
Isobutyl . . .	222·06 ,,	212·83 ,,	9·23 ,,

The mean difference is 9·40 Cal.; the greatest deviation from this being only 0·9 per cent. of the heat of combustion of the substance, which proves that we were justified in making use of the values previously found for the constants v_1 and r.

The general formula for these aldehydes is $C_aH_{2a+1}.COH$. If now we represent by q' the influence exerted by the COH group upon the heat of formation, P, it follows that—

$$P = av_1 + (2a + 1)r + q', \quad . \quad . \quad . \quad (20)$$

and we then find for q' the values given in the fifth column of the table, which is that part of the heat of formation of the aldehyde due to the COH group, namely—

Acetic aldehyde . . .	COH = 65·22 Cal.	64·88 Cal.
Propionic aldehyde . .	= 65·01 ,,	
Isobutyric aldehyde . .	= 64·40 ,,	

Thus the thermal effect corresponding to the COH group is considerably greater than that which was calculated above for the COH group of the corresponding alcohols, namely 44·67 Cal., whence it follows that the constitution must be very different in the two cases (see below).

(*b*) *The ketones and secondary alcohols* stand in the same relation to each other as the aldehydes and primary alcohols; thus methylpropyl ketone corresponds to methylpropyl carbinol. I have not investigated this last alcohol, but have found that the isomeric dimethylethyl carbinol, which is a tertiary alcohol, is in complete agreement with isopropyl

alcohol with respect to its heat of formation. A comparison of the heats of formation of these substances gives the following results :—

Compound.	Heat of formation.	Difference.
Isopropyl alcohol	184·11 Cal.	11·71 Cal.
Dimethyl ketone	172·40 „	
Dimethylethyl carbinol . .	273·22 „	11·92 „
Methylpropyl ketone . .	261·30 „	

Thus the heat of formation of the ketones is also less than that of the corresponding secondary alcohols; the difference, namely 11·82 Cal., is somewhat greater than that between the aldehydes and the primary alcohols, which amounts only to 9·40 Cal.

The ketones contain the C : O group, and the heat of formation of a ketone C_aH_{2a+2}. CO must therefore be

$$P = av_1 + (2a + 2)r + s, \quad . \quad . \quad . \quad (21)$$

where s represents the influence of the CO group upon the heat of formation. We thus find that for

Dimethyl ketone	s = CO = 53·58 Cal.
Methylpropyl ketone . . .	= 53·46 „

the mean value, 53·52 Cal., therefore corresponds to the thermal effect due to the bonds of the oxygen gram-atom in the ketone.

Whilst there is no difference in the heats of formation of the various isomers in a series of hydrocarbons, owing to the fact that the four valencies of the carbon are identical, such a difference is, however, observed in substances belonging to the series under consideration, in which the *isomerism* is due to the different position occupied by the oxygen atom in the molecule. Thus in the three compounds of the formula C_3H_6O we have the following difference in the heats of formation :—

Dimethyl ketone	172·40 Cal.
Propionic aldehyde	168·93 „
Allyl alcohol	144·89 „

(*c*) *Acids.*—The first three members in the fatty acid series, namely, formic, acetic, and propionic acids, which formed the subject of my research, have greater heats of formation, P, than have the corresponding alcohols. The following values were found for P:—

Formic acid	133·73 Cal.	44·77 Cal.
Methyl alcohol . . .	88·96 „	
Acetic acid	180·89 „	47·11 „
Ethyl alcohol	133·78 „	
Propionic acid . . .	222·85 „	44·05 „
Propyl alcohol . . .	178·80 „	

The mean value of 45·31 Cal. gives the difference between the heat of formation of a fatty acid and that of the corresponding alcohol.

The influence which the characteristic COOH group exercises upon the heat of formation of the acids can be deduced in the usual manner. When the formula of the acid is $C_aH_{2a+1}.COOH$, and when t represents the influence of the COOH group, we have

$$P = (2a + 1)r + a.v_1 + t \quad . \quad . \quad . \quad (22)$$

The values of t are found in Table 48, and are as follows:—

Formic acid	COOH = 118·83 Cal.
Acetic acid	= 121·48 „
Propionic acid . . .	= 118·93 „

Thus the average thermal value of the COOH group is 119·75 Cal. Now, we have found above that the CO group in the ketones corresponds to 53·52 Cal., and the COH group in the aldehydes to 64·88 Cal.; we therefore have

$$53{\cdot}52 \text{ Cal.} + 64{\cdot}88 \text{ Cal.} = 118{\cdot}40 \text{ Cal.},$$

which exactly agrees with the value found for the COOH group in formic and propionic acids, namely 118·88 Cal. We may therefore conclude that the *thermal effect corresponding to the COOH group in acids is equal to the sum of the effect due to the COH group in the aldehyde and to the carbonyl, CO, group of the ketones.*

Now, since the carboxyl group has the formula $O:\underset{|}{COH}$, and the carbonyl of the ketone has that of $O:C=$, the aldehydic COH group must have the formula $R.COH$; that is to say, the *aldehydes are unsaturated compounds.*

(*d*) *Acetic anhydride.*—The rational formula of this compound is $H_3C.CO.O.CO.CH_3$; so that besides the six hydrogen atoms united to the carbon atoms the molecule contains the group

$$O:\underset{|}{C}-O-\underset{|}{C}:O.$$

If we represent the thermal value corresponding to the heat of formation of this group by z, the heat of formation must be

$$P = 6r + 2v_1 + z = 284{\cdot}34 \text{ Cal.}$$

Hence it follows that the heat of formation of the group in question is

$$z = 165{\cdot}52 \text{ Cal.}$$

Now, this group contains three atoms of oxygen, which are joined to the carbon atoms by two bonds, and it has been shown above that such a double linkage for the oxygen gram-atom in the ketones and in the acids represents respectively 53·52 and 54·83 Cal., whilst the value of z is $3 \times 55{\cdot}17$ Cal. We may therefore conclude that *the C : O and the C . O . C. groups in acetic anhydride correspond to equal thermal effects.*

(*e*) *Ketones and paraffins.*—A comparison between the heats of formation of the ketones and of the paraffins shows the following interesting relation :—

		P	Difference.
Dimethyl ketone .	$CH_3.CO.CH_3$	172·40 Cal.	68·24 Cal.
Dimethyl . . .	$CH_3.CH_3$	104·16 „	
Methylpropyl ketone	$CH_3.CO.C_3H_7$	261·30 „	67·65 „
Methylpropyl . .	$CH_3.C_3H_7$	193·65 „	

The mean value, 67·94 Cal., exactly corresponds to the heat of formation of carbon monoxide at constant volume, namely 67·67 Cal. Hence it follows that when a paraffin

takes up carbon monoxide, and thereby forms a ketone, the thermal effect is equal to zero, or very nearly so. The bond between the two alkyl radicals of the paraffin is broken and replaced by a bond with the carbon atom of the carbon monoxide; whence it follows that the two radicals are bound to the carbon monoxide molecule with the same strength with which they were bound together in the paraffin.

10. Esters.

A comparison of the heats of combustion of the esters and of the corresponding hydrocarbons shows that these run on parallel lines; whence it follows that the constants which enter into the heats of combustion and of formation of the hydrocarbons also enter into those of the esters. This fact makes it possible to calculate the influence of the grouping characteristic of the esters, and the following table provides us with the necessary data. P, as usual, represents the absolute heat of formation of the compound, calculated from the numbers in column 7 of Table 41 by the addition of 38·38 Cal. for each gram-atom of carbon that the compound contains.

TABLE 50.

HEATS OF FORMATION OF THE ESTERS.

Name.	Molecular formula.	Heat of formation, P	$mr + nv$	$P-(mr+nv)$
		Cal.		Cal.
Dimethyl carbonate	$(CH_3)_2 . CO_3$	251·50	$6r$	162·10
Diethyl carbonate .	$(C_2H_5)_2 . CO_3$	341·21	$10r + 2v_1$	162·79
Methyl formate . .	$CH_3 . O . COH$	165·03	$4r$	105·43
Methyl acetate . .	$CH_3 . O . C_2H_3O$	210·12	$6r + v_1$	106·01
Ethyl formate . .	$C_2H_5 . O . COH$	209·30	$6r + v_1$	105·19
Propyl formate . .	$C_3H_7 . O . COH$	253·68	$8r + 2v_1$	105·06
Methyl isobutyrate .	$CH_3 . O . C_4H_7O$	298·66	$10r + 3v_1$	105·53
Ethyl acetate . .	$C_2H_5 . O . C_2H_3O$	265·91	$8r + 2v_1$	117·29
Methyl propionate .	$CH_3 . O . C_3H_5O$	258·53	$8r + 2v_1$	109·91
Isobutyl formate .	$C_4H_9 . O . COH$	295·70	$10r + 3v_1$	103·57
Allyl formate . .	$C_3H_5 . O . COH$	216·80	$6r + v_2$	99·42

The constants are, as before, $r = 14{\cdot}90$ Cal. and $v_1 = 14{\cdot}71$ Cal.

(*a*) *Esters of carbonic acid.*—The two esters investigated were dimethyl carbonate and diethyl carbonate. The heats of formation of these are 251·50 and 341·21 Cal., and they have the following constitutional formulæ :—

$$H_3C.O.\underset{\underset{O}{\|}}{C}.O.CH_3 \quad \text{and} \quad H_5C_2.O.\underset{\underset{O}{\|}}{C}.O.C_2H_5.$$

If we subtract from the heat of formation the thermal effect which corresponds to the bonds between the hydrogen and carbon atoms—that is, $6r$ and $10r + 2v_1$—we obtain the thermal value corresponding to the formation of the grouping

$$C.O.\underset{\underset{O}{\|}}{C}.O.C,$$

and according to the preceding table this amounts to 162·10 and 162·79 Cal. The group contains three oxygen atoms, each of which is united by two bonds to one or two carbon atoms.

We therefore have the same condition as that investigated above in the case of the ketones, the acids, and of acetic anhydride, where we found that the thermal effect due to each gram-atom of oxygen amounted to

Ketones	53·52 Cal.
Acids	54·83 „
Acid anhydrides	55·17 „

But the heat of formation of the group in question is

$$162{\cdot}44 \text{ Cal.} = 3 \times 54{\cdot}15 \text{ Cal.},$$

which is in complete agreement with the values found above for the bonds of the oxygen atom, so that the heat of formation of the carbonic esters affords additional evidence in favour of the assumption that the formation of the C : O and C—O—C groups is attended by an equal thermal effect, the average value of which may be placed at 54·16 Cal.

(*b*) *Esters of the fatty acids.*—The molecule of the esters derived from a paraffin and a fatty acid contains the group

and the influence of this grouping upon the heat of formation of the molecule can be found in the usual manner, by subtracting from the last-mentioned value the thermal effect due to the bonds between the hydrogen and carbon atoms, as well as those due to the bonds between the carbon atoms themselves. We thus obtain an approximately constant value of from 105·06 to 106·01 Cal., of which the mean is 105·44 Cal.

The two oxygen atoms in the grouping under consideration are both bound by two valencies to either one or two carbon atoms, so that, from what has been said above, the thermal effect corresponding to each oxygen gram-atom should be the same—that is, equal to 52·72 Cal. This also agrees with the values derived above for a similar grouping in the case of the ketones, the acid anhydrides, and the carbonic esters, namely, an average value of 54·16 Cal.

But, on the other hand, there are considerable deviations in the last four esters contained in the table. The greatest of these is the case of *ethyl acetate*, namely, about 12 Cal., or over 2 per cent. of the heat of combustion—a difference which lies far outside the limits of experimental error. I have expended considerable time and labour in the endeavour to explain these deviations.

To satisfy myself that I was working with pure material, I subjected a large quantity of the "purest" commercial ethyl acetate to a systematic fractionation, when the greater part of the distillate had a boiling-point of 76·9° (corrected); whilst former specimens had ranged over from 72·8° to 80°. The first of these boiling-points, namely 72·8°, is stated by Geuther (*Arch. d. Pharm.*, 166, 100) to correspond to a product obtained by the distillation of "pure" ethyl acetate from metallic sodium; but it was my experience that the product so formed was not pure, but contained always some diethyl ether. This

could, however, be removed by systematic fractionation, when the boiling-point rose to about 77°.

I then prepared ethyl acetate *synthetically by the interaction of equivalent amounts of absolute alcohol and glacial acetic acid*, without distillation, the ester formed being subsequently precipitated by addition of water. After being washed and dried, the product had a constant boiling-point of 77·5° (corrected) at 762·5 mm. pressure. Finally, I prepared ethyl acetate by the decomposition of *ethyl iodide by means of silver acetate.* The product thus obtained, after a single distillation, had a constant boiling-point of 77·4° (corrected) at 754·8 mm. pressure.

There can therefore be no doubt but that the *boiling-point of ethyl acetate lies between* 77·4 *and* 77·5°. The vapour of the two synthetically prepared compounds has a heat of combustion of 546·57 ± 0·58 Cal. at 18°, whilst *all the products with lower boiling-points have higher heats of combustion;* that of the product with a boiling-point of 74° was some 20 Cal. higher.

This compound, with a boiling-point of from 77·4° to 77·5°, which must undoubtedly be a definite chemical compound, has a heat of combustion which is 12·23 Cal. lower than that of propyl formate, which is isomeric with ethyl acetate. Now, since the heat of formation is thus 12·23 Cal. greater than the calculated value, the *constitution of ethyl acetate must be different from that of the other five esters investigated*, and of which the heats of formation are perfectly regular. I have made numerous experiments with a view to gaining some information as to the possible constitution of ethyl acetate; these are described in *Therm. Unters.*, iv. p. 310.

11. Halogen Compounds.

The absolute heats of formation of the halogen compounds are found in the same manner as those of the hydrocarbons, by the addition of $a \times 38{\cdot}38$ Cal. to the numbers in the seventh column of Table 36; the values so found are given in the following table under the heading *P*. Since the heats of formation of these compounds do not run parallel to those of the hydrocarbons, the values of the constants r and v_1 which

enter into the calculation must also differ somewhat from those previously found; and that this is the case will now be shown.

(*a*) *Chlorides.*—If P_1 represents the heat of formation of the first member of a series of homologous compounds, then the following terms will be

$$P_a = P_1 + (a - 1)(2r + v_1),$$

where the difference in composition is CH_2; r represents, as before, the thermal effect due to the bond between one half-molecule of hydrogen and an atom of carbon.

For the first four chlorides the calculation gives the following probable values for the constants P_1 and $v_1 + 2r$:—

$$P_1 = k + 3r = 60{\cdot}57 \text{ Cal.}$$
$$v_1 + 2r = 45{\cdot}35 \text{ ,,}$$

where k represents the thermal effect due to the bond between an atom of chlorine (half-molecule) and one of carbon. We thus have

Molecule.	Heat of formation, P, at constant volume.		Difference.
	Experimental.	Calculated.	
CH_3Cl	60·35 Cal.	60·57 Cal.	+0·22
C_2H_5Cl	106·31 ,,	105·92 ,,	−0·39
C_3H_7Cl	151·16 ,,	151·27 ,,	+0·11
C_4H_9Cl	196·57 ,,	196·62 ,,	+0·05

In order to determine the magnitude of the three constants k, r, and v_1, we can make use of the heats of formation of the three compounds, CH_3Cl, $CHCl_3$, and CCl_4, namely—

for CH_3Cl	60·35 Cal.	$= k + 3r$
$CHCl_3$	61·91 ,,	$= 3k + r$
CCl_4	58·83 ,,	$= 4k$
Total	181·09 Cal.	$= 8k + 4r$

Comparing this result with that found above—that is

$$k + 3r = 60{\cdot}57 \text{ Cal.} = 4 \times 15{\cdot}14 \text{ Cal.}$$
$$v_1 + 2r = 45{\cdot}35 \text{ ,,} = 3 \times 15{\cdot}12 \text{ ,,}$$
$$2k + r = 45{\cdot}27 \text{ ,,} = 3 \times 15{\cdot}09 \text{ ,,}$$

it is evident that there is no appreciable difference between

the values of the three constants, so that we shall not introduce any sensible error by taking them as equal; we then have

$$k = r = v_1 = 15{\cdot}13 \text{ Cal.}$$

I must, however, remind the reader of what was said on p. 397, where, as I pointed out in a similar relationship in the case of the hydrocarbons, the apparent equality must not be taken as absolute, but merely as indicating that there is no great difference in magnitude between these constants. In the present instance there are not sufficient data to determine with certainty any possible differences in the values of the constants. In the calculation of k in Table 51, v_2, as before, was taken as equal to 13·27 Cal., and the nine bonds of the phenyl radical, or $9u$, according to the determination on p. 395, as 126·81 Cal. The value of k—that is to say, the thermal effect due to the linkage between an atom (half-molecule) of chlorine and an atom of carbon—appears as the difference between the value of P and of that made up of the sum of the bonds between the carbon atoms themselves and of those between the carbon and hydrogen atoms.

TABLE 51.

HEATS OF FORMATION OF THE CHLORIDES.

Molecule.	P Heat of formation.	n Number of bonds.	
	Cal.		Cal.
CH_3Cl	60·35	$3r$	$k = 14{\cdot}96$
C_2H_5Cl	106·31	$5r + v_1$	15·53
C_3H_7Cl	151·16	$7r + 2v_1$	14·99
C_4H_9Cl	196·57	$9r + 3v_1$	15·01
C_6H_5Cl	217·90	$5r + 9u$	15·44
C_2H_3Cl	74·30	$3r + v_2$	15·64
C_3H_5Cl (propylene)	122·39	$5r + v_2 + v_1$	18·34
C_3H_5Cl (allyl)	121·08	$5r + v_2 + v_1$	17·03
$CH_2Cl.CH_2Cl$	109·88	$4r + v_1$	$2k = 34{\cdot}23$
$CH_3.CHCl_2$	109·83	$4r + v_1$	34·18
$CH_3.CCl_2.CH_3$	155·48	$6r + 2v_1$	34·44
$CHCl_3$	61·91	r	$3k = 46{\cdot}78$
$C_2H_3Cl_3$	109·58	$3r + v_1$	49·06
CCl_4	58·83		$4k = 58{\cdot}83$
C_2Cl_4	75·03	v_2	61·76

It is evident from the last column in the table that in the first four alkyl chlorides the gram-atom of chlorine is bound with a strength which corresponds to 15·12 Cal., and this is the exact value which was ascribed to r and v_1; that is to say, that due to the bonds between the hydrogen and carbon atoms and between the carbon atoms themselves. This same magnitude applies also to the linkages of the chlorine atoms in the last two chlorides in the table, namely CCl_4 and C_2Cl_4, which contain four atoms of carbon in the molecule, since the mean value is $4 \times 15{\cdot}08$ Cal. In the case of the other compounds the introduction of chlorine into the molecule produces a somewhat greater thermal effect; the highest value being found for the three saturated chlorides with two atoms of chlorine in the molecule, namely $2 \times 17{\cdot}14$ Cal. The explanation of this deviation is not easy to see, but it is evident that the chlorides $C_2H_4Cl_2$ and $C_2H_3Cl_3$ have equal heats of formation, namely 109·85 and 109·58 Cal. respectively, so that

$$2k + 4r + v_1 = 3k + 3r + v_1 = 109{\cdot}72 \text{ Cal.},$$

and it is therefore practically certain that also in the chlorides with two and three atoms of chlorine the value of the bonds is the same—that is, 15·68 Cal.—for each one of them; whilst for the chlorides with one, and probably also for those with four, atoms of chlorine in the molecule, the value is about 0·5 Cal. lower.

It should also be noted that the isomeric chlorides, monochlorpropylene and allyl chloride, and similarly ethylene chloride and ethylidene chloride, have equal heats of formation, so that the position of the chlorine atom in the molecule does not influence its heat of formation.

(*b*) *Bromides and iodides.*—The following table contains the heats of formation at constant volume of the bromides and iodides compared with those of the chlorides. The heats of formation are calculated *for both bromine and iodine in the state of vapour at* 18°, so that the values are directly comparable with those determined for chlorine.

TABLE 52.

HEATS OF FORMATION OF THE BROMIDES AND IODIDES.

Radical.	Heat of formation, P, at constant volume.		
	Chloride.	Bromide.	Difference.
Methyl . . .	60·35 Cal.	52·59 Cal.	7·76 Cal.
Ethyl . . .	106·31 ,,	98·60 ,,	7·71 ,,
Propyl . . .	151·16 ,,	144·25 ,,	6·91 ,,
Allyl . . .	121·08 ,,	113·64 ,,	7·44 ,,
		Iodide.	
Methyl . . .	60·35 ,,	41·22 ,,	19·13 ,,
Ethyl . . .	106·31 ,,	86·69 ,,	19·62 ,,

Thus the heats of formation of the bromides are 7·45 Cal., and those of the iodides 19·38 Cal., lower than the heats of formation of the chlorides; and this difference may very possibly be connected with the unequal strength with which the three halogens are bound to the carbon atom. Now, since we found above that the linking of the chlorine gram-atom to a carbon gram-atom corresponded to a thermal effect of 15·13 Cal., therefore the values of the bonds for the three halogens must be

Carbon and chlorine	15·13 Cal.
,, ,, bromine gas . .	7·68 ,,
,, ,, iodine vapour .	−4·25 ,,

These numbers, which also in a measure correspond to the degree of affinity between carbon and the three halogens, call to mind the heats of formation of the hydrides of these substances, which at 18° amount to (see p. 191)

$$(H, Cl) = 22{\cdot}00 \text{ Cal.}$$
$$(H, Br_{gas}) = 12{\cdot}26 \text{ ,,}$$
$$(H, I_{gas}) = -0{\cdot}67 \text{ ,,}$$

The affinity of carbon is, however, somewhat lower than that of hydrogen for the same halogen.

12. Ethers and Acetals.

The molecules of the oxides of alcohol radicals and of mixed ethers are supposed to be composed of two alcohol radicals united by an atom of oxygen, and to correspond to the formula $C_aH_b . O . C_aH_\beta$. The heat of formation of the molecule will therefore be

$$P = (b + \beta)r + q + \Sigma v,$$

where q represents the thermal effect which accompanies the linking of the two radicals to oxygen.

The absolute heats of formation, as well as those obtained by the addition of $(a + \alpha)38{\cdot}38$ Cal. to the experimental results given in the seventh column of Table 37, will be found below in Table 53. If now we compare some of these numbers with the heats of formation of the corresponding chlorides (Table 51), we arrive at a very remarkable result. Thus we have

Compound.	Molecule.	Heat of formation, P	Difference.
Dimethyl ether . .	$CH_3 . OCH_3$	124·95 Cal.	64·60 Cal.
Methyl chloride . .	$CH_3 . Cl$	60·35 ,,	
Ethylmethyl ether .	$C_2H_5 . OCH_3$	171·56 ,,	65·25 ,,
Ethyl chloride . . .	$C_2H_5 . Cl$	106·31 ,,	
Allylmethyl ether . .	$C_3H_5 . OCH_3$	185·57 ,,	64·49 ,,
Allyl chloride . . .	$C_3H_5 . Cl$	121·08 ,,	
Phenylmethyl ether .	$C_6H_5 . OCH_3$	282·49 ,,	64·59 ,,
Phenyl chloride . .	$C_6H_5 . Cl$	217·90 ,,	

There is therefore a constant difference between the heats of formation of these analogous compounds, and from this we may conclude that it is possible to calculate the heats of formation of the ethers by means of the same constants made use of in the case of the chlorides; that is to say—

$$r = v_1 = 15{\cdot}13 \text{ Cal.} \qquad v_2 = 13{\cdot}27 \text{ Cal.} \qquad v_3 = O,$$

and for the nine bonds of the phenyl radical we have, as before, 126·81 Cal. If now we subtract from the absolute heat of formation, P, in Table 53, the value of the collective linkages

between the carbon atoms, and between these latter and the hydrogen atoms, we obtain the thermal effect corresponding to the formation of the C . O . C group, which is given in the fourth column of the table. These values agree very satisfactorily, with the single exception of that of diethyl ether, and, omitting this last number, we obtain a mean value of 34·31 Cal. for the remaining seven ethers. The total heat of formation of the ether C_aH_b . O . $C_\alpha H_\beta$. is thus

$$P = (b + \beta) . 15{\cdot}13 \text{ Cal.} + \Sigma v + 34{\cdot}31 \text{ Cal.}$$

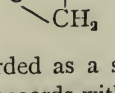
TABLE 53.

ETHERS AND ACETALS.

Name.	Molecule $C_aH_b . O . C_\alpha H_\beta$	Heat of formation at constant volume.	COC
Dimethylene ether (ethylene oxide)	$CH_2 . O . CH_2$	93·98 Cal.	33·46 Cal.
Dimethyl ether . .	$CH_3 . O . CH_3$	124·95 ,,	34·17 ,,
Methylethyl ether. .	$CH_3 . O . C_2H_5$	171·56 ,,	34·59 ,,
Diethyl ether . . .	$C_2H_5 . O . C_2H_5$	220·95 ,,	41·39 ,,
Methylpropargyl ether	$CH_3 . O . C_3H_3$	141·16 ,,	35·25 ,,
Methylallyl ether . .	$CH_3 . O . C_3H_5$	185·57 ,,	36·13 ,,
Diallyl ether . . .	$C_3H_5 . O . C_3H_5$	240·13 ,,	32·03 ,,
Methylphenyl ether (anisol)	$CH_3 . O . C_6H_5$	282·49 ,,	34·64 ,,
Methylal	$C_3H_8O_2$	201·06 ,,	See p. 417
Methyl orthoformate	$C_4H_{10}O_3$	280·79 ,,	

From the numbers given in the table we can draw some conclusions as to the constitution of ethylene oxide.

The molecule of *ethylene oxide* is usually assumed to correspond to the formula



that is to say, it is regarded as a saturated compound. This, however, by no means accords with the heat of formation of 93·98 Cal. derived from its heat of combustion, which is about 14·70 Cal. lower than the value required to correspond to the

preceding formula. If, on the other hand, we represent the molecule of the compound by the formula

$$H_2C.O.CH_2,$$

that is, as *dimethylene ether*, this would agree with a heat of formation

$$P = 4 \times 15{\cdot}13 \text{ Cal.} + 34{\cdot}31 \text{ Cal.} = 94{\cdot}83 \text{ Cal.},$$

which differs only by 0·85 Cal. from the experimental result. Dimethylene oxide has therefore two free valencies, and this is in accordance with the ease with which it combines with other substances, as, for example, water, whilst the saturated ethers are very indifferent substances. The compound thus appears to be dimethylene ether.

Methylal and methyl orthoformate.—These compounds, corresponding to the formulæ $C_3H_8O_2$ and $C_4H_{10}O_3$, might possibly, similarly to dimethyl ether, C_2H_6O, be regarded as derivatives of methane, in which one, two, or three atoms of hydrogen are replaced by the $O.CH_3$ group. But a comparison of the heats of formation of these compounds does not support this view. The heats of formation of the four compounds are as follows:—

		Difference.
CH_4	59·55 Cal.	65·40 Cal.
$CH_3(OCH_3)$	124·95 „	76·11 „
$CH_2(OCH_3)_2$	201·06 „	79·73 „
$CH(OCH_3)_3$	280·79 „	

Thus, if we accepted the above-mentioned formulæ, the substitution of the successive OCH_3 groups for the hydrogen atoms would be attended by an appreciable difference in thermal effect, and this is in opposition to the supposed identity of the four valencies of the carbon atom.

If, on the other hand, we regard these two compounds as hydroxy-derivatives of methylethyl ether and diethyl ether, a relation between the thermal values at once becomes apparent, since the heats of formation are

			Difference.
Methylal	$C_3H_8O_2$	201·06 Cal.	1 × 29·50 Cal.
Methylethyl ether . .	C_3H_8O	171·56 „	
Methyl orthoformate .	$C_4H_{10}O_3$	280·79 „	2 × 29·92 „
Diethyl ether	$C_4H_{10}O$	220·95 „	

This difference of 29·71 Cal. for each gram-atom of oxygen taken up is in exact agreement with the difference between the heats of formation of an alcohol and the corresponding paraffin, namely 29·77 Cal., and it is therefore probable that the two compounds contain one or two oxygen atoms in the form of hydroxyl, and thus agree with the formulæ

$$CH_3 . O . \underset{OH}{CH} . CH_3 \text{ and } CH_3 . \underset{OH}{CH} . O . \underset{OH}{CH} . CH_3$$

13. Thermal Effect due to the Dissociation of Molecules into Atoms.

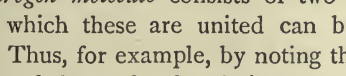
(*a*) *The carbon molecule.*—It has been demonstrated by numerous examples in the preceding pages that two carbon atoms cannot be bound together with a strength greater than that which corresponds to the so-called *single* bond, but that owing to its polyvalence the carbon atom is enabled to combine with other carbon atoms, to each of which it is united with a strength not exceeding that of a single bond between two atoms. In a complex carbon molecule, consisting of five or more atoms, such as the molecule of solid carbon may be assumed to be, each atom of carbon is able to bind four other atoms with the same strength, so that the total number of bonds in the molecule will be double the number of its atoms. It is this strong attraction which has to be overcome before the carbon atom can be dissociated from the solid substance and enter into a chemical compound. But in order to convert the atoms thus liberated into the gaseous state, a further amount of energy must be supplied.

Experiments have shown that the total energy necessary to produce the conditions under which the atoms corresponding to twelve parts by weight of solid amorphous carbon can enter

into a gaseous compound amounts to 38·38 Cal., whilst the thermal effect corresponding to two single bonds is 29·42 Cal., so that 8·96 Cal. are expended in bringing about the gaseous condition.

Now it is highly probable that a similar relation holds in the case of other polyvalent atoms; that is to say, *two polyvalent atoms of the same element are always bound together with a strength not exceeding that which corresponds to a "single bond,"* independently of whether we represent the bond as single or manifold.

(*b*) *The nitrogen molecule* consists of two atoms, and the strength with which these are united can be calculated in several ways. Thus, for example, by noting the thermal effect on dissociation of the molecule of nitrogen tetroxide, which may be assumed to have the following formula :—



In each case, when the bond between the two nitrogen atoms is broken, two molecules of are produced.

The thermal effect due to this dissociation was measured by Berthelot and Ogier (*Ann. Chim. Phys.*, (5) xxx. 397), over a temperature interval of from 27° to 198°, when they found that the heat absorbed amounted to 10·61 Cal. per gram-molecule; but since at 27° some 20 per cent. of the substance is already dissociated, the heat of dissociation of the non-dissociated gram-molecule, N_2O_4, will be 13·25 Cal. This value was also determined by L. Boltzmann (*Wiedermann's Annalen* (2) xxii. 71), who found 13·92 Cal.; the mean value can therefore be placed at 13·60 Cal. But since the dissociation of one molecule gives rise to two molecules, *the heat of dissociation at constant volume* is

$$13{\cdot}60 \text{ Cal.} - 0{\cdot}58 \text{ Cal.} = 13{\cdot}02 \text{ Cal.}$$

As already mentioned, I make use of *small letters to represent the isolated atoms* whenever there is any possibility of confusion,

so that *the heat of formation of* 1 *gram-molecule of nitrogen* will be

$$n \cdot n = 13{\cdot}02 \text{ Cal.},$$

and this corresponds to the heat of dissociation of 1 gram-molecule of N_2O_4.

(*c*) *The affinity of nitrogen for hydrogen.*—The thermal effect on formation of 1 gram-molecule of NH_3 I found to be 11·89 Cal. at constant pressure, or 11·31 Cal. at constant volume. If now we add to this $\frac{1}{2}n \cdot n$, or 6·51 Cal., we obtain—

$$(n, H_3) = 17{\cdot}82 \text{ Cal.};$$

that is to say, when a free nitrogen gram-atom unites with hydrogen to form ammonia, the thermal effect is 17·82 Cal.; and since we may assume that the thermal value of each atom (or of each half-molecule) of hydrogen is the same, we obtain

$$(n, H) = 5{\cdot}94 \text{ Cal. and } (n, H_2) = 11{\cdot}88 \text{ Cal.},$$

whence it again follows that—

$NH_3 = 11{\cdot}31$ Cal., $NH_2 = 5{\cdot}37$ Cal., and $NH = -0{\cdot}57$ Cal.

are the heats of formation of the groups of atoms in question when molecular nitrogen is taken as the starting-point.

(*d*) *The heat of formation of nitrogen tetroxide* when measured directly by the oxidation of nitric oxide, *NO*, with free oxygen, was proved to be 39·14 Cal. for the reaction $(2NO, O_2)$, and the solution in water of the red vapours of partially dissociated nitrogen tetroxide thus formed produced a thermal effect of 15·51 Cal. The sum of these two observations gives—

$$(2NO, O_2Aq) = 54{\cdot}65 \text{ Cal.}$$

This result is correct, but the magnitude of the two components is influenced by the partial dissociation of nitrogen tetroxide at the temperature of the experiment, since without dissociation these values would have been 40·50 Cal. and 14·15 Cal. respectively; the sum of the numbers will, of course, be the same. From these numbers we can deduce the heats of formation of N_2O_4 and NO_2 in the pure state—

		At constant pressure.	At constant volume.
Nitrogen tetroxide .	(N_2, O_4)	−2·650 Cal.	−3·810 Cal.
Nitric peroxide . .	(N, O_2)	−8·125 „	−8·415 „

These values have already been given on p. 252.

(*e*) *Heat of dissociation of the oxygen molecule.*—If we assume that the molecule of nitrogen peroxide has the formula—

and that two similar polyvalent atoms are always united with the same strength—that is, with a thermal effect corresponding to that of the single bond, as we have shown it to be in the case of the carbon atom—then we can deduce the heat of formation of the oxygen molecule from a comparison of the heats of formation of NO and NO_2.

Representing the free atoms by means of small letters, we have the following two equations, valid for the reactions at constant volume :—

$$(N, O) = -21{\cdot}575 \text{ Cal.} = n : o - \tfrac{1}{2}\, n.n - \tfrac{1}{2}\, o.o$$
$$(N, O_2) = -8{\cdot}515 \text{ „} = 2n.o - \tfrac{1}{2}\, n.n.$$

If now, on the preceding assumption, we put

$$n : o = 2n.o,$$

we then obtain—

$$(N, O_2) - (N, O) = 13{\cdot}16 \text{ Cal.} = \tfrac{1}{2} o.o\,;$$

that is to say, the *heat of formation of a gram-molecule of oxygen* must be

$$o : o = 26{\cdot}32 \text{ Cal.}$$

Comparing this number with that given by Boltzmann in the above-mentioned publication for the *heat of dissociation of the iodine molecule*, namely 28·52 Cal. at constant pressure, and therefore 27·94 Cal. at constant volume, we obtain the following noteworthy results :—

$$c.c = 14{\cdot}71 \text{ Cal.}$$
$$n.n = 13{\cdot}02 \text{ „}$$
$$o.o = 2 \times 13{\cdot}16 \text{ „}$$
$$i.i = 2 \times 13{\cdot}97 \text{ „}$$

Hence we must conclude that the thermal values of the bonds between the homogeneous atoms of a gaseous molecule are multiples of a common constant; or, in other words, that the heats of dissociation of the molecules of gaseous elements are multiples of a constant magnitude, equal to about 13·60 Cal.

14. Nitriles and Cyanides.

(*a*) *Nitriles.*—The two homologues that I investigated were acetonitrile and propionitrile, and it is quite easy to calculate the share that the C⋮N grouping, characteristic of the nitriles, takes in the heat of formation. The thermal effect on formation of these two nitriles from the atoms of hydrogen, nitrogen, and carbon is respectively 60·50 Cal. and 104·31 Cal., and is made up of the following terms:

$$H_3C.C\vdots N = 3r + v_1 + c\vdots N = 60{\cdot}50 \text{ Cal.} = A$$
$$H_5C_2.C\vdots N = 5r + 2v_1 + c\vdots N = 104{\cdot}31 \text{ „} = B$$

We thus have

$$2A - B = r + c\vdots N = 16{\cdot}69 \text{ Cal.}$$

If now we put r—that is to say, the thermal value of the bond uniting a half gram-molecule of hydrogen to carbon—at 14·90 Cal., as in the case of the hydrocarbons, we obtain—

$$c\vdots N = 1{\cdot}79 \text{ Cal.} = c\vdots n - \tfrac{1}{2}\, n.n;$$

and this value, 1·79 Cal., is valid for molecular nitrogen. Now since, as we have found above, the formation of the gram-molecule of nitrogen from its atoms is attended by a thermal effect, $n.n = 13{\cdot}02$ Cal., the thermal effect of formation of the $c\vdots n$ group will be

$$1{\cdot}79 \text{ Cal.} + 6{\cdot}51 \text{ Cal.} = 8{\cdot}30 \text{ Cal.} = c\vdots n,$$

which is a comparatively low value.

(*b*) *Cyanogen.*—Whilst there can be no doubt but that the constitution of the nitriles must be that attributed to them above, much uncertainty still prevails as to the configuration of the cyanogen molecule; that is, should the formula be N⋮C . C⋮N or C : N − N : C. From the heat of formation

of the cyanogen gram-molecule, namely 11·06 Cal., it is evident that the first of these formulæ cannot be the correct one, since if it were so we should have

$$N \vdots c \,.\, c \vdots N = v_1 + 2N \vdots c = 11{\cdot}06 \text{ Cal.}$$

But since $v_1 = 14{\cdot}71$ Cal., the formation of the N⋮c group should correspond to a thermal value of $-1{\cdot}82$ Cal., whilst we found above, in the case of the nitriles, a value of $+1{\cdot}79$ Cal. for this group. If, on the other hand, we assume that the cyanogen molecule has the formula c : N − N : c—that is to say, that each of the atoms in the nitrogen molecule is united to a carbon atom—we shall have

$$c : N - N : c = 2c : n = 11{\cdot}06 \text{ Cal.},$$

since the molecule of nitrogen has not been decomposed.

This value is in complete agreement with that found for the $c \vdots n$ group in the nitriles, namely, 8·30 Cal. for $c \vdots n$, since

$$2 \times c : n = 11{\cdot}06 \text{ Cal.} = 4 \times 2{\cdot}77 \text{ Cal.}$$
$$c \vdots n = \quad 8{\cdot}30 \quad \text{„} \quad = 3 \times 2{\cdot}77 \quad \text{„}$$

that is to say, the thermal effect corresponding to the triple bond $c \vdots n$ between the carbon and nitrogen atoms of the nitriles is one and a half times as great as that due to the double bond $c : n$ of cyanogen. We may therefore assume that the constitution of the cyanogen molecule is C : N − N : C, and also that a *single bond between a carbon and a nitrogen gram-atom corresponds to a thermal value of* 2·77 *Cal.*

(*c*) *Hydrogen cyanide.*—It is evident from their heats of formation that the nitriles and hydrogen cyanide do not belong to the same series of homologous compounds. Thus we find

Hydrogen cyanide . .	10·90 Cal.	49·60 Cal.	5·79 Cal.
Acetonitrile	60·50 „	43·81 „	
Propionitrile . . .	104·31 „		

Whilst the difference between the heats of formation of the nitriles is 43·81 Cal., and therefore corresponds to the common difference between the members of a homologous series, the value for hydrogen cyanide, on the other hand, differs by 49·60 Cal. from that of acetonitrile.

There are two formulæ which might be attributed to the molecule of hydrogen cyanide, namely, either HCN or HNC. The heat of formation is 10·90 Cal., and if we add to this $\frac{1}{2}n \,.\, n$, or 6·51 Cal., we obtain 17·41 Cal. for the formation of the gram-molecule from hydrogen and free atoms of carbon and nitrogen. Supposing the constitution of the molecule to be HNC, then the heat of formation must be (see p. 420)

$$17{\cdot}41 \text{ Cal.} - n \,.\, H + nc = 5{\cdot}94 \text{ Cal.} + nc,$$

and this gives a value of 11·47 Cal. for nc, which is far higher than the value found above for the triple linkage $c \vdots n$, namely 8·30 Cal. If, on the other hand, we accept the second formula, HCN, then the heat of formation will be

$$17{\cdot}41 \text{ Cal.} = r + nc = 14{\cdot}90 \text{ Cal.} + nc,$$

from which we find $nc = 2{\cdot}51$ Cal. This is a very close approximation to the value of 2·77 Cal. found above for the single bond, and we are therefore justified in assigning the formula HC.N to the molecule of hydrogen cyanide, which differs by an amount equal to 2c.n from the $n \vdots c$ group of the nitriles.

Since the first two determinations gave completely concordant values for $c \,.\, n$, and the third differs only by a small amount, I have placed the value of the single linkage between a nitrogen and a carbon atom at

$$c \,.\, n = 2{\cdot}77 \text{ Cal.},$$

and represent the molecules of the three substances investigated by

HC.N C:N − N:C $H_3C.C \vdots N.$

That dissimilar atoms can be united by their valencies in various ways has already been noted above in the case of oxygen, for it was shown that the formation of the groupings C:O and C—O—C gave equal thermal effects (see p. 408 and also Table 54).

15. Ammonia and the Amines.

The investigation comprised 13 amines in all, including the primary, secondary, and tertiary methyl- and ethylamines; and in addition propyl-, isobutyl-, and amylamine, as well as allylamine, aniline, pyridine, and piperidine.

(*a*) *The general character of the heat of formation* is the same as that previously observed, namely, that the differences between the heats of formation of two successive members in a series of homologous compounds of the same constitution are equal to one another. This is shown in Table 54, where the following magnitudes are given for the heats of formation, P:—

		Difference.
Methylamine	46·76 Cal.	1 × 45·77 Cal.
Ethylamine	92·53 „	
Dimethylamine . . .	87·74 „	2 × 46·10 „
Diethylamine . . .	179·94 „	
Trimethylamine . . .	128·69 „	3 × 46·54 „
Triethylamine . . .	268·30 „	

The difference comes out a little greater than in the majority of the series already described, but a similar relation was nevertheless observed in the case of the halogen compounds and ethers.

Isomeric amines, such as ethylamine and dimethylamine, show, on the other hand, differences in their heats of formation arising from their dissimilar constitution; for example—

Ethylamine	92·53 Cal.	4·79 Cal.
Dimethylamine	87·74 „	
Propylamine	135·56 „	6·87 „
Trimethylamine	128·69 „	

so that the heats of formation of the primary amines are greater than those of their secondary and tertiary isomers.

The primary, secondary, and tertiary amines of the same

radical, however, exhibit equal differences in their heats of formation, thus—

		Difference.
Methylamine	46·76 Cal.	
		40·98 Cal.
Dimethylamine	87·74 „	
		40·95 „
Trimethylamine	128·69 „	
Ethylamine	92·53 „	
		87·41 „
Diethylamine	179·94 „	
		88·44 „
Triethylamine	268·30 „	

(*b*) *The constitution of the amines* is usually deduced from that of ammonia. They are regarded as derivatives of ammonia, in the molecule of which one, two, or three atoms of hydrogen are replaced by alkyl radicals. But this assumption is not in accordance with the heats of formation, which for ammonia at constant volume is 11·31 Cal., so that the differences are

Methylamine − Ammonia = 35·46 Cal.
Ethylamime − Ammonia = 81·22 „

and these values are considerably lower than the differences between the other amines belonging to the same series, which are respectively 40·97 and 87·92 Cal. These facts can only be explained on the supposition either that the hydrogen atoms in ammonia have not all the same value, which is highly improbable, or else that the constitution attributed to the primary amines does not hold good in every case.

If we assume that the amines are formed from ammonia and the corresponding hydrocarbon with the elimination of a molecule of hydrogen—that is, in accordance with the equation

$$C_aH_{2b} + NH_3 - H_2 = C_aH_{2b+1}N,$$

this reaction will be attended by a thermal effect determined by

$$(C_a, H_{2b+1}, N) - (C_a, H_{2b}) - (N, H_3) = R$$
$$P_1 - P - 11{\cdot}31 \text{ Cal.} = R$$

The values of R are given in the table below.

Hydrocarbon.	P	Amine.	P_1	R
	Cal.		Cal.	Cal.
Methane	59·55	Methylamine	46·76	−24·10
Ethane	104·16	Ethylamine	92·53	−22·94
Propane	148·31	Propylamine	135·56	−24·26
Pentane	236·85	Amylamine	226·98	−21·18
Benzene	216·61	Aniline	211·09	−16·83
Propylene	117·20	Allylamine	112·26	−16·25
C_5H_{10}	221·00	Piperidine	215·99	−16·32
Isobutane	193·65	Isobutylamine	189·08	−15·88

It is obvious that we have here amongst the so-called primary amines two series with different constitutions; the mean value of the heats of reaction in the first series is 23·12 Cal., in the second 16·32 Cal.

In a similar manner the heat of formation can be determined for a reaction in which a primary or secondary amine takes part in the place of ammonia, and in which there is consequently formed either a secondary or a tertiary amine. Thus we find

Dimethylamine − (Methane + Methylamine) = −18·57 Cal.
Trimethylamine − (Methane + Dimethylamine) = −18·60 „
Diethylamine − (Ethane + Ethylamine) = −16·75 „
Triethylamine − (Ethane + Diethylamine) = −15·80 „

The mean value is in this case 17·43 Cal., and thus approximates very closely to that of the heat of reaction, namely 16·32 Cal., found for the second series of the amines; on the other hand, it diverges widely from the mean value of the first group, which is 23·12 Cal. We may therefore conclude that in the last two series the reaction is the same, but that it is different in the first series.

In this connection it is noteworthy that the *heats of neutralization of ammonia and the amines* also point to a difference in constitution. The evolution of heat per gram-molecule on

neutralization of dilute solutions by means of hydrochloric acid amounts to

Ammonia	12,270 Cal.
Methylamine	13,115 „
Dimethylamine . . .	11,810 „
Trimethylamine . . .	8,740 „

Thus the heat of neutralization *rises* with the introduction of the first CH_2 group into the molecule of ammonia, but *falls*, on the other hand, for each of the two following. This would be very remarkable behaviour on the assumption that the introduction of each of the three CH_2 groups produced a similar change in the configuration of the ammonia molecule.

It is evident from the preceding statements that the constitution of the amines differs according to whether they belong to the first or to the second of the above-mentioned series; thus, for example, the formulæ $CH_3.NH_2$ and $C_6H_5.NH_2$ cannot both correspond to the actual constitutions of methylamine and aniline respectively. Now, as the constitution of aniline, as deduced from its heat of formation and from the configuration of benzene, cannot be other than that usually assigned to it, namely $C_6H_5.NH_2$, we must therefore seek for some other formula for methylamine and its analogues.

If now we compare the heats of formation of the two compounds $CH_3.NH_2$ and $CH_2:NH_3$, making use of the values already known to us, namely—

$r = 14{\cdot}90$ Cal.	$c.n = 2{\cdot}77$ Cal.
$NH_2 = 5{\cdot}37$ „	$NH_3 = 11{\cdot}31$ „

we find for

$$CH_3.NH_2 \quad 3r + n.c + NH_2 = 52{\cdot}84 \text{ Cal.}$$
$$CH_2:NH_3 \quad 2r + 2n.c + NH_3 = 46{\cdot}65 \text{ „}$$

whilst the experimental value for the heat of formation of methylamine equals 46·76 Cal. It is therefore scarcely open to doubt but that its constitution must be $CH_2:NH_3$. Hence it follows that the constitution of the secondary and tertiary methylamines must be

$$H_2C:NH_3 \quad \left.\begin{matrix} H_2C: \\ H_3C. \end{matrix}\right\} NH_2 \quad \left.\begin{matrix} H_2C: \\ H_3C. \\ H_3C. \end{matrix}\right\} NH;$$

that is to say, the *nitrogen atom in these allied amines is pentavalent.* The great similarity in behaviour between the primary amines of this series and ammonia when treated with nitrous acid also appears to support the suggested constitution.

In Table 54 I have collected together the heats of formation of all the nitriles and amines examined. As in the former tables, the heats of formation are given for the formation of the compounds from free atoms of carbon, and also the values derived from the numbers in column 7 of Table 43 by the addition of 38·38 Cal. for each gram-atom of carbon in the compound. At the same time, the tables contain the components of the heats of formation, namely, the thermal effect corresponding to the atoms directly united to the nitrogen atom, which are dependent upon the three constants previously determined—

$c.n = 2{\cdot}77$ Cal. $\quad n.n = 13{\cdot}02$ Cal. $\quad (N, H_3) = 11{\cdot}31$ Cal.

Hence we can deduce the thermal values of the groups of atoms represented in the table, namely—

C . N = −3·74 Cal.	C : NH_3 = 16·85 Cal.
C : N = −0·97 ,,	C ⋮ NH_2 = 13·68 ,,
C ⋮ N = +1·80 ,,	C :: NH = 10·51 ,,
C :: N = +4·57 ,,	C . NH_2 = 8·14 ,,

These are the values designated in the table by the letter *Q*. The thermal effect due to the bonds between the carbon atoms themselves is, as in the case of the hydrocarbons and other compounds, placed at 14·71 Cal. for v_1 and at 13·27 Cal. for v_2 in the aliphatic series (see p. 391), and at 14·09 Cal. for *u* in aromatic compounds (see p. 395).

If we subtract *Q*, and also the thermal value corresponding to the linkages between the carbon atoms, from the heat of formation, *P*, we have left that part of the thermal effect due to the hydrogen atoms of the compound which are united to the carbon. This is the value which has previously been

represented by r, and which in the case of the hydrocarbons, alcohols, aldehydes, ketones, acids, etc., amounts to 14·90 Cal., whilst for the halogen compounds and ethers it has a somewhat higher value, namely, from 15·19 to 15·67 Cal.

TABLE 54.

HEATS OF FORMATION OF THE CYANIDES, NITRILES, AND AMINES.

Name.	$C_aH_bC_c$	Heat of formation at constant volume.	
		P	$=Q+br+nv$
		Cal.	
Cyanogen . . .	$C:N-N:C$	11·06	$=2C:N+nn$
Hydrogen cyanide	$HC.N$	10·90	$=C.N+1\times14{\cdot}64$
Acetonitrile . .	$H_3C.C:N$	60·50	$=C:N+4\times14{\cdot}68$
Propionitrile . .	$H_5C_2.C:N$	104·31	$=C:N+7\times14{\cdot}64$
Methylamine . .	$H_2C:NH_3$	46·76	$=C:NH_3+2\times14{\cdot}95$
Dimethylamine .	$\left.\begin{matrix}H_2C:\\H_3C.\end{matrix}\right\}NH_2$	87·74	$=C:NH_2+5\times14{\cdot}81$
Trimethylamine .	$\left.\begin{matrix}H_2C:\\H_3C.\\H_3C.\end{matrix}\right\}NH$	128·69	$=C::NH+8\times14{\cdot}77$
Ethylamine . .	$H_4C_2:NH_3$	92·53	$=C:NH_3+4\times15{\cdot}24+v_1$
Diethylamine . .	$\left.\begin{matrix}H_4C_2:\\H_5C_2.\end{matrix}\right\}NH_2$	179·94	$=C:NH+9\times15{\cdot}20+2v_1$
Triethylamine. .	$\left.\begin{matrix}H_4C_2:\\H_5C_2.\\H_5C_2.\end{matrix}\right\}NH$	268·30	$=C::NH+14\times15{\cdot}26+3v_1$
Propylamine . .	$H_6C_3:NH_3$	135·56	$=C:NH_3+6\times14{\cdot}88+2v_1$
Amylamine . .	$H_{10}C_5:NH_3$	226·98	$=C:NH_3+10\times15{\cdot}13+4v_1$
Isobutylamine. .	$H_9C_4.NH_2$	189·08	$=C.NH_2+9\times15{\cdot}21+3v_1$
Allylamine. . .	$H_5C_3.NH_2$	112·26	$=C.NH_2+5\times15{\cdot}23+\left\{\begin{matrix}v_1\\v_2\end{matrix}\right.$
Phenylamine . .	$H_5C_6.NH_2$	211·09	$=C.NH_2+5\times15{\cdot}23+9u$
Piperidine . . .	$H_9C_5.NH_2$	215·99	$=C.NH_2+9\times15{\cdot}27+5u$
Pyridine . . .	$H_5C_5.N$	171·37	$=C.N+5\times15{\cdot}29+7u$

It is evident from the table that the value of r, or the thermal effect corresponding to each of the hydrogen atoms which is united to a carbon atom, is in exact agreement for each of the series in question; and, moreover, that the constitution of the eight amines corresponding to the normal paraffins is in complete accordance with that given above for the primary, secondary, and tertiary amines. On the other

hand, the constitution of isobutylamine and of allylamine must be assumed to be $C_4H_9 . NH_2$ and $C_3H_5 . NH_2$—that is, similar to that of aniline, namely $C_6H_5 . NH_2$.

The explanation of this must be looked for in the constitution of the corresponding hydrocarbons—

$$H_3C—\underset{CH_3}{\overset{H}{C}}—CH_3 \text{ and } H_3C—\overset{H}{C} = CH_2,$$

in which the NH_2 group attaches itself to that carbon atom which is already combined with the least number of hydrogen atoms (as is also the case in the reaction between hydrochloric acid and the unsaturated hydrocarbons), so that the constitution of these amines can be represented by

$$H_3C—\underset{CH_2}{\overset{NH_2}{C}}—CH_3 \text{ and } H_3C—\overset{NH_2}{C} = CH_2,$$

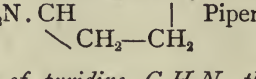
which is thus analogous to that of aniline, $C_6H_5 . NH_2$.

(*c*) *Pyridine and piperidine.*—The molecule of pyridine is usually supposed to have a constitution similar to that of benzene, only that an atom of nitrogen replaces one of the trivalent CH groups. But the heat of formation of pyridine is not compatible with this view, no matter whether we adopt the Kekulé formula for benzene, or assume a constitution with nine single linkages. In the first case the heat of formation of the gram-molecule would be 132·27 Cal., in the second 160·85 Cal. But neither of these values accords with the heat of formation of pyridine as deduced from its heat of combustion, namely 171·37 Cal.

The constitution of pyridine is therefore not derived from that of benzene, but from that of a hydrocarbon, C_5H_6, the carbon atoms of which are linked by seven single bonds; that is to say, with the greatest possible number which a saturated hydrocarbon of the formula C_5H_6 can have. Now, when one atom of hydrogen is replaced by an atom of nitrogen, we have for the constitution of *pyridine*

$$N . \begin{matrix} \diagup CH—CH \\ CH \quad >\!\!<\!| \\ \diagdown CH—CH \end{matrix} \quad \text{Pyridine,}$$

and from this we can, in the usual manner, derive the constitution of *piperidine*, which contains six additional atoms of hydrogen, whereby two single linkages are destroyed; thus we have



Piperidine.

The molecule of pyridine, C_5H_5N, therefore contains seven linkages between the carbon atoms, that of piperidine, on the other hand, only five, and the data in Table 54 show that the experimental results are in support of this hypothesis. The fact that we can derive from piperidine both a dimethylpiperidine and also a trimethylpiperyllium iodide is in satisfactory agreement with the presence of the NH_2 group in the piperidine molecule.

16. Nitro-compounds, Nitrites, and Nitrates.

(*a*) *The constitution of nitro-compounds.*—A comparison of the heats of formation of nitromethane and of nitroethane with those of the corresponding chlorides shows the following constant difference :—

	Heat of formation.	Difference.
$CH_3 . Cl$	60·35 Cal.	4·53 Cal.
$CH_3 . NO_2$	55·82 „	
$C_2H_5 . Cl$	106·31 „	4·41 „
$C_2H_5 . NO_2$	101·90 „	

We may therefore conclude that the same constants enter into the heats of formation of the two series, and that consequently both for the nitro-compounds and also for the chlorides we can put r and v_1 equal to 15.13 Cal. Furthermore, $c.n = 2{\cdot}77$ Cal. (see p. 423) and $(N, O_2) = -8{\cdot}12$ Cal. (see p. 252).

The formula commonly accepted for the nitro compounds is $R . NO_2$, where R represents the alcohol radical. The heat of formation of such a compound would be as follows (see Table 55) :—

	Calculated.	Experimental.
$(C, H_3, N, O_2) = 3r + n.c + (N, O_2)$	=40·10 Cal.	55·82 Cal.
$(C_2, H_5, N, O_2) = 5r + n.c + (N, O_2) + v_1$	=85·55 „	101·90 „

There is therefore a difference of 15·72 and 16·35 Cal. between the experimental and calculated results, from which it is apparent that *the accepted constitution of the nitro-compounds, namely $R.NO_2$, cannot be the correct one.*

Since the observed heat of formation is so much higher than that calculated according to the formula $R.NO_2$, it follows that a part of the oxygen must be linked to carbon; that is to say, the molecule contains the NO and not the NO_2 group. If, however, we regard these so-called nitro-compounds as *nitroso-derivatives of the alcohols, in which an atom of hydrogen is replaced by NO*, the discrepancy between the theoretical and practical values disappears, and the formulæ become

$$\begin{array}{cc} H & H \\ H.C.OH & H_3C.C.OH \\ NO & NO \end{array}$$

The heats of formation of these compounds can be calculated by means of the same constants that were made use of in former examples, and by putting the COH group equal to the value found for the alcohols, namely 44·42 Cal. (see p. 400), and (N, O) equal to the thermal effect determined for the formation of 1 gram-molecule of NO—that is, −21·57 Cal. (see p. 252); but 0·29 Cal. must be added to this last value, since the replacement of an atom of hydrogen in the alcohol molecule by a molecule of NO produces a contraction of half a molecular volume.

The heats of formation of the two nitro-, or, more properly speaking, nitroso-compounds, are as follows:—

	Calculated.	Experimental.
$2r+COH+c.n+(N,O)+0·29$ Cal. =	56·17 Cal.	55·82 Cal.
$v_1+4r+COH+c.n+(N,O)+0·29$ „ =	101·56 „	101·90 „

The difference between the experimental and calculated values amounts only to ±0·34 Cal., and this is a negligible quantity, being only some 0·1 to 0·2 per cent. of the heats of combustion of the compounds, namely 180·90 and 337·94 Cal.

It is easy to explain several of the characteristic properties of the nitro-compounds on the supposition that they are substituted alcohols in which a hydrogen atom of the radical

has been replaced by NO, but the explanation is less satisfactory if we accept the formula $R.NO_2$. Thus on substitution of a hydrogen atom by bromine or NO, the primary compounds form derivatives in which the acidic properties are even more pronounced than in the original substances. These three compounds can be represented by the following formulæ :—

$$\begin{array}{ccc} H & Br & NO \\ CH_3.C.OH & CH_3.C.OH & CH_3.C.OH \\ NO & NO & NO \end{array}$$

On the other hand, the secondary nitro-compounds form indifferent substances on substitution by bromine; for example—

$$\begin{array}{cc} CH_3 & CH_3 \\ CH_3.C.OH & CH_3.C.OBr; \\ NO & NO \end{array}$$

where the resulting products do not contain a hydroxyl group. The tertiary compounds are known not to have a hydrogen atom joined to the CNO group, and consequently do not form bromine derivatives corresponding to those described above.

Similarly, we can explain the *formation of hydroxylamine from nitromethane* when acted upon by concentrated hydrochloric acid in the following simple manner: one molecule of water is decomposed, and there is an interchange between the H and NO constituents of the H.C.NO group and the oxygen atoms of the water, thus giving rise to a fatty acid, whilst the hydrogen atoms of the water join up with the H and NO to form hydroxylamine, H_3NO.

Now, since the general properties of the *nitro-compounds*, as well as their heats of formation, are satisfactorily explained on the assumption that they are *substituted alcohols with an NO group in place of one of the hydrogen atoms* of the alcohol radical, there is every reason to believe that this assumption is justified.

(*b*) *Nitrites and nitrates.*—The heats of formation of the nitrites cannot be determined with any great degree of accuracy, owing to their very unstable nature.

TABLE 55.

NITRO-COMPOUNDS, NITRITES, AND NITRATES.

Name.	Rational formula.	Heat of formation, P, at constant volume.	
		Experimental.	Calculated (see text).
		Cal.	
Nitromethane .	$HO.CH_2.NO$	55·28	56·17 Cal.
Nitroethane . .	$HO.C_2H_4.NO$	101·90	101·56 ,,
Ethyl nitrite . .	$C_2H_5.O.NO$	105·63	37·99 ,,
Amyl nitrite . .	$C_5H_{11}.O.NO$	236·56	*c.o.n* 35·39 ,,
Ethyl nitrate . .	$C_2H_5.O.NO_2$	115·51	34·71 ,,

These substances are esters in which the acid radical is NO or NO_2. Their rational formulæ will therefore, for example, be $H_5C_2.O.NO$ and $H_5C_2.O.NO_2$. They all contain the *c.o.n* group of atoms, and the share this grouping takes in the heat of formation of the compound can be calculated in the usual manner by inserting the constants r and v_1, which as before are taken as equal to 14·90 and 14·71 Cal., and also the values for NO and NO_2, which were given above as −21·57 and −8·41 Cal. We thus have for

		Cal.	*c.o.n* Cal.
$C_2H_5.O.NO$	$5r + v_1 + NO + c.o.n =$	$67·64 + c.o.n$	37·99
$C_5H_{11}.O.NO$	$11r + 4v_1 + NO + c.o.n =$	$201·17 + c.o.n$	35·39
$C_2H_5.O.NO_2$	$5r + v_1 + NO_2 + c.o.n =$	$80·80 + c.o.n$	34·71

The values found for *c. o. n.* vary somewhat considerably, although not more than was to be expected from the nature of the compounds, which makes accurate measurements of the heats of combustion a very difficult matter.

17. Sulphur Compounds.

The thermal effect on formation of sulphur compounds is always calculated starting from *rhombic sulphur*, of which the heat of combustion is 71·08 Cal. It was not considered worth while to determine the value for the vapour of sulphur, since its heat of vaporization is not accurately known.

The heats of formation of the *mercaptans and disulphides* run parallel to those of the series already described, as will be apparent from the following comparison between the heats of formation of certain of these compounds :—

	Methyl.	Ethyl.	Difference.
Mercaptan . .	43·75 Cal.	90·03 Cal.	46·28 Cal.
Disulphide . .	2 × 44·16 „	2 × 89·87 „	2 × 45·71 „
Amine . . .	46·76 „	92·53 „	45·77 „
Chloride . . .	60·35 „	106·31 „	45·96 „

The mean value of these differences, namely 45·88 Cal., is somewhat higher than that between two members of the paraffin series (44·51 Cal.); but here again we can make use of the same constants as in the case of the chlorides, and put $r = v_1 =$ 15·13 Cal. If now with the help of these constants we calculate the influence of the C . S . H and C . S . C groups for the first four compounds, we arrive at the numbers given in the fourth column of Table 56, namely − 1·20 and − 1·80 Cal. respectively. The influence is thus very small and negative.

TABLE 56.

MERCAPTANS, SULPHIDES, SULPHOCYANIDES, ETC.

Substance.	Molecular formula.	Heat of formation, P, at constant volume.	
		Cal.	
Hydrogen sulphide . .	H . SH	2·73	
Methyl mercaptan . .	CH_3 . SH	43·75	CSH { −1·64 Cal.
Ethyl mercaptan . . .	C_2H_5 . SH	90·03	CSH { −0·75 „
Dimethyl sulphide . .	$(CH_3)_2S$	88·33	CSC { −1·80 „
Diethyl sulphide . . .	$(C_2H_5)_2S$	179.75	CSC { −1·81 „
Carbon disulphide . .	CS_2	12·95	C : S +6·47 „
Carbonyl sulphide . .	COS	75·70	
Thiophene	C_4H_4S	137·94	
Methyl sulphocyanide .	CH_3 . S . NC	44·77	see text
Methyl isosulphocyanide	CH_3 . NCS	51·66	see text
Allyl isosulphocyanide .	C_3H_5 . NCS	106·82	see text

Since the heat of formation of *carbon disulphide* is 12·95 Cal., the thermal effect corresponding to the C : S group must be 6·47 Cal., whilst we found above in the case of the sulphides a value of −1·80 Cal. for the C . S . C group of atoms. This agrees very well with the results of the investigation of the ethers, where it was found that the C. O . C group corresponded to a thermal effect of 34·31 Cal., whilst the C : O group of the dioxide and monoxide of carbon had a far higher value, namely 67·67 Cal.

Carbonyl sulphide, COS, forms, as it were, a sort of connecting link between carbon dioxide and carbon disulphide, and its heat of formation should therefore lie between those of these two substances. The experimental values are

	Heat of combustion.	Absolute heat of formation.
Carbon dioxide . . .	0·0 Cal.	135·34 Cal.
Carbonyl sulphide . .	131·01 „	75·70 „
Carbon disulphide . .	265·13 „	12·95 „

so that the heat of formation of carbonyl sulphide falls but slightly higher than the mean value of the other two numbers. This difference is, however, no greater than might be explained by an error of ± 0·6 per cent. in the heat of combustion. We thus obtain the values 74·92 and 14·50 Cal. for the heats of formation of the two compounds, and consequently a difference of 60·42 Cal. between C : O and C : S. Now, since C : O corresponds to 67·67 Cal., C : S must be equal to 7·25 Cal., whilst the experimental result was 6·48 Cal.

Thiophene.—Special interest is attached to the heat of formation of thiophene, namely 137·94 Cal., since the value gives us some insight into the constitution of the substance. This is usually derived from the Kekulé formula for benzene, in the molecule of which the CH : CH group is supposed to be replaced by S, just as the pyridine molecule is assumed to be derived from benzene by replacing the trivalent CH group by an atom of nitrogen. But as in the case of pyridine, so also in that of thiophene, the heat of formation is not compatible with this assumption.

According to the Kekulé formula the molecule of thiophene, C_4H_4S, in addition to the four hydrogen atoms linked to carbon, should contain two double and one single bond between the atoms of carbon themselves, as well as the $c.S.c$ group of atoms. Now, if we put $v_1 = v_2 = 14{\cdot}09$ Cal., as corresponding to the linkages in the aromatic radical, and $r = 15{\cdot}13$ Cal. as before, the heat of formation should be

$$v_1 + 2v_2 + 4r + c.S.c = 102{\cdot}79 \text{ Cal.} + c.S.c,$$

whilst the experimental result is 137·94 Cal. And since we found above that $c.S.c$ was equal to $-1{\cdot}80$ Cal., there is a difference of 36·94 Cal. between the observed and theoretical values, which shows that the Kekulé formula must be rejected.

Thiophene can, however, be derived from a saturated hydrocarbon, C_4H_6, with five single bonds between the carbon atoms, if we suppose that two atoms of hydrogen are replaced by an atom of sulphur. According to this theory, the thiophene molecule would have the following constitution :—

$$S : C\begin{array}{c}CH\\ <|>\\ CH\end{array}CH_2.$$

If we accept this formula, the heat of formation of thiophene per gram-molecule will be

$$5v_1 + 4r + c : S = 130{\cdot}97 \text{ Cal.} + c : S.$$

Now, the heat of formation of a gram-molecule of CS_2 is equal to 12·94 Cal., so that the formation of the C : S group must be attended by a thermal effect of 6·47 Cal. If we add this value to 130·97 Cal., we obtain 137·45 Cal. as the heat of formation of a gram-molecule of thiophene, and this is in exact agreement with the experimental result. There can therefore be no doubt that the formula which I have attributed to thiophene is the correct one, and that its molecule is derived from a saturated hydrocarbon, C_4H_6, with five single linkages, in which two atoms of hydrogen are replaced by an atom of sulphur.

18. Tabular Comparison of the Heats of Combustion and of Formation of Volatile Organic Compounds.

The following tables contain the numerical results of my researches on the thermal properties of 120 organic substances, arranged in systematic order.

In the third column are given the results of direct experiment; that is to say, the *heats of combustion at constant pressure* corresponding to the gram-molecular weight of the compounds, when the *products of combustion* are as follows, namely: *gaseous* carbon dioxide, nitrogen, sulphur dioxide, and chlorine, the *vapours* of bromine and iodine (at 18°), and *liquid* water.

Combustion at constant pressure is accompanied by a change in volume, because the sum of the volumes of the compound and of the oxygen necessary to its combustion will usually be either greater or less than the sum of the volumes of the products. The energy corresponding to the change in volume is equal to 0·58 Cal. for each gram-molecular volume which disappears at 18°. A part of the observed heat of combustion is consequently a result of the change in volume, and this must naturally be allowed for in arriving at the true heat of combustion; that is to say, that found at constant volume.

The fourth column contains a statement of the change in volume resulting from the combustion; this, for the compounds in question, is expressed in terms of n half-molecular volumes, and its influence will accordingly be $n \times 0{\cdot}29$ Cal. This magnitude must be subtracted from the actual experimental result in order to arrive at the *heat of combustion at constant volume.* Thus, for example, one gram-molecule of methane with two gram-molecules of oxygen produces only one gram-molecule of carbon dioxide; the contraction is thus two gram-molecular volumes, and the correction will be $4 \times 0{\cdot}29$ Cal., or 1·16 Cal.; if this be subtracted from 211·93 Cal., we obtain 210·77 Cal. as the heat of combustion of methane at constant volume, and so on.

The heats of formation of the respective compounds follow from their heats of combustion, since they are equal to the differences between the heats of formation of the products of

the combustion and the heats of combustion of the compounds themselves; for example—

$$(C_a, H_{2b}, S) = a(C, O_2) + b(H_2, O) + (S, O_2) - f. C_aH_{2b}S.$$

In all cases the *heats of formation* given refer to amorphous carbon, rhombic sulphur, molecular gaseous hydrogen, nitrogen, and chlorine, and to the vapours of bromine and iodine. The following are the values used for the heats of formation of carbon dioxide, water, and sulphur dioxide :—

$(C, O_2) = 96{\cdot}96$ Cal.
$(S, O_2) = 71{\cdot}08$ „
$(H_2, O) = 68{\cdot}36$ Cal. at constant pressure
$(H_2, O) = 67{\cdot}49$ „ „ volume.

In the third column of the following tables are given the *heats of combustion at constant pressure*, since these are the actual experimental measurements, and they moreover provide a means of direct comparison with the results of other experimenters. On the other hand, the fifth column contains the *heats of formation at constant volume*, which must be used in all cases when considering their relations one to another. These values are represented by p, and are calculated according to the preceding equation, in which the heat of combustion of the compound and the heat of formation of water are both taken at constant volume; for example we have for

$$(C_2, H_6) = 2 \times 96{\cdot}96 \text{ Cal.} + 3 \times 67{\cdot}49 \text{ Cal.} - (370{\cdot}44 \text{ Cal.} - 5 \times 0{\cdot}29 \text{ Cal.})$$

$$(C_2, H_6) = p = 27{\cdot}40 \text{ Cal.}$$

The values represented by p in the fifth column may be described as the *empirical heats of formation*, since they refer to a special condition of the carbon, namely, the amorphous variety, with a heat of combustion of 96·96 Cal.

On the other hand, the values in the sixth column represent the heats of formation of the respective compounds with reference to the atom of carbon. The thermal effect resulting from the union of a gram-atom of carbon with oxygen to form carbon dioxide is here taken as equal to 135·34 Cal.—that is to say, twice the value of the heat of combustion of carbon monoxide (at constant volume this equals 67·67 Cal.)—and this value corresponds to the heat of combustion of a carbon atom taken as the constituent of a gaseous compound. The heats of

formation calculated in this manner are 38·38 Cal. greater than the empirical values for each gram-atom of carbon in the gram-molecule of the compound; for a compound with a gram-atoms of carbon in the molecule, we thus have

$$P = p + a \times 38{\cdot}38 \text{ Cal.}$$

The magnitude P represents the *absolute heat of formation.* From this we can easily learn the relation between the heat of formation and the constitution of the compound, as, for example, by making use of the empirical heat of formation, which corresponds to the formation of the substance from amorphous carbon.

The numbers in the tables all refer to the molecular weights of the compounds, and the thermal values are expressed in kilogram-calories.

TABLE 57.

HEATS OF COMBUSTION AND OF FORMATION OF VOLATILE ORGANIC COMPOUNDS.

Substance.	Molecular formula.	Heat of combustion at constant pressure.	n	Heat of formation at constant volume.	
				p	P
		Cal.		Cal.	Cal.
HYDROCARBONS.					
Methane	CH_4	211·93	4	21·17	59·55
Ethane	C_2H_6	370·44	5	27·40	104·16
Propane	C_3H_8	529·21	6	33·37	148·51
Trimethylmethane	$CH(CH_3)_3$	687·19	7	40·13	193·65
Tetramethylmethane	$C(CH_3)_4$	847·11	8	44·95	236·85
Di-isopropyl	$(C_3H_7)_2$	999·20	9	57·60	287·88
Benzene	C_6H_6	799·35	5	−13·67	216·61
Toluene	C_7H_8	955·68	6	− 5·26	263·40
Mesitylene	C_9H_{12}	1282·31	8	− 2·41	343·01
Pseudocumene	C_9H_{12}	1281·51	8	− 1·59	343·83
Ethylene	C_2H_4	333·35	4	− 3·29	73·47
Propylene	C_3H_6	492·74	5	+ 2·06	117·20
Trimethylene	C_3H_6	499·43	5	− 4·63	110·51
Isobutylene	C_4H_8	650·62	6	+ 8·92	162·44
Isoamylene	C_5H_{10}	807·63	7	+16·65	208·55
Diallyl	C_6H_{10}	932·82	7	−11·58	218·70
Acetylene	C_2H_2	310·05	3	−47·77	28·99
Allylene	C_3H_4	467·55	4	−40·53	74·61
Dipropargyl	C_6H_6	882·88	5	−97·20	133·08

Substance.	Molecular formula.	Heat of combustion at constant pressure.	n	Heat of formation at constant volume.	
				p	P
		Cal.		Cal.	Cal.
Halogen Compounds.					
Methyl chloride	CH_3Cl	176·95	$\frac{5}{2}$	21·97	60·35
Ethyl chloride	C_2H_5Cl	334·11	$\frac{7}{2}$	29·55	106·31
Propyl chloride	C_3H_7Cl	492·38	$\frac{9}{2}$	36·02	151·16
Isobutyl chloride	C_4H_9Cl	650·09	$\frac{11}{2}$	43·05	196·57
Monochlorethylene	C_2H_3Cl	298·34	$\frac{5}{2}$	− 2·46	74·30
Monochlorpropylene	C_3H_5Cl	453·37	$\frac{7}{2}$	+ 7·25	122·39
Allyl chloride	C_3H_5Cl	454·68	$\frac{7}{2}$	+ 5·94	121·08
Phenyl chloride	C_6H_5Cl	763·88	$\frac{7}{2}$	−12·38	217·90
Ethylene chloride	$C_2H_4Cl_2$	296·36	2	+33·12	109·88
Ethylidene chloride	$C_2H_4Cl_2$	296·41	2	33·07	109·83
Dichlorpropane	$C_3H_6Cl_2$	453·88	3	40·34	155·48
Carbonyl chloride	$COCl_2$	41·82	−1	54·85	93·23
Chloroform	$CHCl_3$	107·03	$-\frac{1}{2}$	23·53	61·91
Monochlorethylene chloride	$C_2H_3Cl_3$	262·48	$+\frac{1}{2}$	32·82	109·58
Perchlormethane	CCl_4	75·93	−2	20·45	58·83
Perchlorethylene	C_2Cl_4	195·07	−2	− 1·73	75·03
Methyl bromide	CH_3Br_{gas}	184·71	$\frac{5}{2}$	+14·21	52·59
Ethyl bromide	$C_2H_5Br_{gas}$	341·82	$\frac{7}{2}$	21·84	98·60
Propyl bromide	$C_3H_7Br_{gas}$	499·29	$\frac{9}{2}$	29·11	144·25
Allyl bromide	$C_3H_5Br_{gas}$	462·12	$\frac{7}{2}$	− 1·50	113·64
Methyl iodide	CH_3I_{gas}	196·08	$\frac{5}{2}$	2·84	41·22
Ethyl iodide	$C_2H_5I_{gas}$	353·73	$\frac{7}{2}$	9·93	86·69
Ethers, etc.					
Ethylene oxide	$CH_2.O.CH_2$	312·55	3	17·22	93·98
Dimethyl ether	$CH_3.O.CH_3$	349·36	4	48·19	124·95
Methylethyl ether	$CH_3.O.C_2H_5$	505·87	5	56·42	171·56
Diethyl ether	$C_2H_5.O.C_2H_5$	659·60	6	67·43	220·95
Methylallyl ether	$CH_3.O.C_3H_5$	627·20	5	32·05	185·57
Diallyl ether	$C_3H_5.O.C_3H_5$	911·10	6	9·85	240·13
Methylpropargyl ether	$CH_3.O.C_3H_3$	603·83	4	−12·36	141·16
Anisol	$CH_3.O.C_6H_5$	936·30	5	+13·83	282·49
Methylal	$CH_2(OCH_3)_2$	476·08	4	85·92	201·06
Trimethylmethenyl ether (Methyl orthoformate)	$CH(OCH_3)_3$	599·18	4	127·27	280·79
Alcohols.					
Methyl alcohol	$CH_3.OH$	182·23	3	50·58	88·96
Ethyl alcohol	$C_2H_5.OH$	340·53	4	57·02	133·78
Propyl alcohol	$C_3H_7.OH$	498·63	5	63·66	178·80
Isopropyl alcohol	$C_3H_7.OH$	493·32	5	68·97	184·11
Isobutyl alcohol	$C_4H_9.OH$	658·49	6	68·54	222·06
Trimethyl carbinol	$C_4H_9.OH$	641·34	6	85·69	239·21
Isoamyl alcohol	$C_5H_{11}.OH$	820·07	7	71·70	263·60

Substance.	Molecular formula.	Heat of combustion at constant pressure.	n	Heat of formation at constant volume	
				p	P
		Cal.		Cal.	Cal.
Dimethylethyl carbinol	$C_5H_{11}.OH$	810·45	7	81·32	273·22
Allyl alcohol	$C_3H_5.OH$	464·76	4	29·75	144·89
Propargyl alcohol	$C_3H_3.OH$	431·10	3	− 4·37	110·77
Phenol	$C_6H_5.OH$	768·76	4	+16·63	246·91
Ethylene glycol	$C_2H_4(OH)_2$	298·11	3	99·15	175·91
Aldehydes and Ketones.					
Acetic aldehyde	$CH_3.COH$	281·90	3	47·87	124·60
Propionic aldehyde	$C_2H_5.COH$	440·72	4	53·79	168·93
Isobutyric aldehyde	$C_3H_7.COH$	599·90	5	59·31	212·83
Dimethyl ketone	$CO(CH_3)_2$	437·25	4	57·26	172·43
Methylpropyl ketone	$CH_3.COC_3H_7$	754·19	6	69·40	251·30
Acids and Anhydrides.					
Formic acid	$H.CO_2H$	69·39	1	95·35	133·73
Acetic acid	$CH_3.CO_2H$	225·35	2	104·13	180·89
Propionic acid	$C_2H_5.CO_2H$	386·51	3	107·71	222·85
Acetic anhydride	$(C_2H_3O)_2O$	460·07	2	130·82	284·34
Esters.					
Methyl formate	$CH_3.CHO_2$	241·21	2	88·27	165·03
Methyl acetate	$CH_3.C_2H_3O_2$	399·24	3	94·98	210·12
Ethyl formate	$C_2H_5.CHO_2$	400·06	3	94·16	209·30
Methyl propionate	$CH_3.C_3H_5O_2$	553·95	4	105·01	258·53
Ethyl acetate	$C_2H_5.C_2H_3O_2$	546·57	4	112·39	265·91
Propyl formate	$C_3H_7.CHO_2$	558·80	4	100·16	253·68
Methyl isobutyrate	$CH_3.C_4H_7O_2$	716·94	5	106·76	298·66
Isobutyl formate	$C_4H_9.CHO_2$	719·90	5	103·80	295·70
Allyl formate	$C_3H_5.CHO_2$	527·90	3	63·28	216·80
Dimethyl carbonate	$(CH_3)_2.CO_3$	357·57	2	136·36	251·50
Diethyl carbonate	$(C_2H_5)_2.CO_3$	674·10	4	149·31	341·21
Ethyl nitrate	$C_2H_5.NO_3$	324·04	½	38·75	115·51
Sulphur Compounds, Mercaptans, etc.					
Hydrogen sulphide	$H.SH$	136·71	3	2·73	2·73
Methyl mercaptan	$CH_3.SH$	298·81	4	5·37	43·75
Ethyl mercaptan	$C_2H_5.SH$	455·65	5	13·27	90·03
Dimethyl sulphide	$(CH_3)_2S$	457·35	5	11·57	88·33
Diethyl sulphide	$(C_2H_5)_2S$	772·17	7	26·23	179·75
Methyl sulphocyanide	$CH_3.S.NC$	398·95	[illegible]	−31·99	44·77
Methyl isosulphocyanide	$CH_3.N.CS$	392·06	[illegible]	−25·10	51·66
Allyl isosulphocyanide	$C_3H_5.N.CS$	675·36	[illegible]	−46·70	106·82
Thiophene	C_4H_4S	610·04	4	−15·58	137·94
Carbon bisulphide	CS_2	265·13	2	−25·43	12·95
Carbonyl sulphide	COS	131·01	1	+37·32	75·70

Substance.	Molecular formula.	Heat of combustion at constant pressure.	n	Heat of formation at constant volume.	
				p	P
		Cal.		Cal.	Cal.
Hydrogen Cyanide and Nitriles.					
Cyanogen	C_2N_2	259·62	0	−65·70	11·06
Hydrogen cyanide	$H.CN$	158·62	$\frac{3}{2}$	−27·48	10·90
Acetonitrile	$CH_3.CN$	312·14	$\frac{5}{2}$	−16·26	60·50
Propionitrile	$C_2H_5.CN$	471·45	$\frac{7}{2}$	−10·83	104·31
Amines.					
Ammonia	NH_3	90 65	$\frac{5}{2}$	11·31	11·31
Methylamine	$CH_3.NH_2$	258·32	$\frac{7}{2}$	8·38	46·76
Dimethylamine	$(CH_3)_2.NH$	420·46	$\frac{9}{2}$	10·98	87·74
Trimethylamine	$(CH_3)_3.N$	582·63	$\frac{11}{2}$	13·55	128·69
Ethylamine	$C_2H_5.NH_2$	415·67	$\frac{9}{2}$	15·77	92·53
Diethylamine	$(C_2H_5)_2.NH$	734·50	$\frac{13}{2}$	26·42	179·94
Triethylamine	$(C_2H_5)_3.N$	1052·38	$\frac{17}{2}$	38·02	268·30
Propylamine	$C_3H_7.NH_2$	575·74	$\frac{11}{2}$	20·42	135·56
Isobutylamine	$C_4H_9.NH_2$	725·36	$\frac{13}{2}$	35·56	189·08
Amylamine	$C_5H_{11}.NH_2$	890·58	$\frac{15}{2}$	35·08	226·98
Allylamine	$C_3H_5.NH_2$	531·28	$\frac{9}{2}$	− 2·88	112·26
Aniline	$C_6H_5.NH_2$	838·47	$\frac{9}{2}$	−19·19	211·09
Pyridine	$C_5H_5.N$	675·07	$\frac{7}{2}$	−20·53	171·37
Piperidine	$C_5H_9.NH_2$	833·79	$\frac{13}{2}$	+24·09	215·99
Nitro-compounds, Nitrites, and Nitrates.					
Nitromethane	$CH_3.NO_2$	180·90	$\frac{1}{2}$	17·44	55·82
Nitroethane	$C_2H_5.NO_2$	337·94	$\frac{3}{2}$	25·14	101·90
Ethyl nitrite	$C_2H_5.O.NO$	334·21	$\frac{3}{2}$	28·87	105·63
Amyl nitrite	$C_5H_{11}.O.NO$	812·64	$\frac{9}{2}$	44·66	236·56
Ethyl nitrate	$C_2H_5.O.NO_2$	324·04	$\frac{1}{2}$	38·75	115·51

CHAPTER XV

REVIEW OF THE THEORETICAL RESULTS BASED UPON RESEARCHES ON THE THERMAL PHENOMENA OF VOLATILE ORGANIC SUBSTANCES

WHILE the atomic and molecular theories are based upon a study of the composition and chemical properties of gaseous substances, the mechanical theory of heat is the outcome of a knowledge of their physical properties. It was therefore an obvious conclusion that an investigation of the thermal effect due to the chemical reactions between gaseous substances would also lead to results of very general application; and it was for this reason that in studying the thermal phenomena of organic substances I directed my attention mainly to the case of volatile compounds.

The research is based upon the determination of the heats of combustion of the volatile compounds, for only very few of the reactions between organic substances take place under conditions suitable to a measurement of the thermal effect on formation of these same substances from their elements.

The heats of combustion were all, as far as possible, carried out in a uniform manner, with the same apparatus and under the same external conditions, and the experimental results were all calculated for the same temperature and physical condition, in order that the results might be directly comparable; for we may assume that all the measurements possess an approximately equal degree of accuracy. Unfortunately, this is not the case with many of the numerical data of other investigators, and *I have consequently based my conclusions exclusively upon the results of my own individual researches.*

The most important theoretical conclusions deduced from a study of the numerical results of the determinations described in the last chapter may be briefly summed up as follows :—

1. In a series of homologous compounds the heat of combustion rises from member to member by an approximately equal amount. In the case of the hydrocarbons, alcohols, aldehydes, ketones, and esters, the mean value of this constant is 158·57 Cal., whilst for the halogen compounds, nitriles, amines, acids, ethers, sulphides, and nitro-compounds, it has a somewhat lower value, namely 157·11 Cal. This magnitude is not an absolute constant, any more than are the majority of physical constants; it must therefore be regarded only as an approximate expression of the influence which the addition of the CH_2 group exercises upon the heat of combustion of a compound.

2. The atoms in a molecule react in the main only upon those atoms with which they are united, so that the heat of formation of a molecule is very closely dependent upon the linkages of the atoms. The constant difference referred to in the preceding paragraph between the heats of combustion, and necessarily also the heats of formation, of two adjacent members in a series of homologous compounds, suggests that the influence of the incoming CH_2 group is not appreciably affected by the atoms to which it united; for in that case there would be a considerable difference in thermal effect, according to whether the group of atoms entered into a molecule which contained oxygen or chlorine, or into a hydrocarbon. It is true that, as mentioned above, a trifling difference in thermal effect was observed, corresponding to the introduction of the CH_2 group into the molecules belonging to different groups of compounds, but the difference is very small in proportion to what it would be it the influence of more distant atoms were to come into play. The heat of formation of a molecule is thus in all essentials derived from the linkages between its atoms, as has been proved by numerous examples in the preceding pages.

3. The four valencies of carbon are identical. A comparison between the heats of combustion of methane and the

four hydrocarbons, ethane, propane or dimethylmethane, trimethylmethane, and tetramethylmethane, shows that the heat of combustion rises by an equal amount for each CH_3 group which enters into the molecule of methane in place of an atom of hydrogen. The four atoms of hydrogen must therefore be bound with equal strength.

It is likewise evident that isomeric chlorides, such as the chlorides of ethylene and ethylidene, allyl chloride and monochlorpropylene, have equal heats of formation, notwithstanding that in the case of ethane and propylene the hydrogen atoms which are replaced by chlorine occupy different positions in the molecule.

Whilst the substitution of a hydrogen atom by CH_3 always produces the same thermal effect, the value will be different when the hydrogen is replaced by the OH group. Thus primary alcohols have a lower heat of formation than their secondary isomers, and these latter a still lower value than the tertiary alcohols; but this relation is no doubt due to the more or less central position of the OH group in the different alcohols, owing to which the influence of the oxygen atom upon the more distant hydrogen or carbon atoms may become considerable, and all the more so since the affinity of oxygen for carbon and hydrogen is far greater than that of any other element (see p. 453).

4. The heat of combustion of a hydrocarbon can be expressed by the following general equation :—

$$fC_aH_{2b} = ax + 2by - \Sigma v, \quad . \quad . \quad . \quad (1)$$

in which x represents the heat of combustion of each of the carbon atoms in the molecule, y that part of the heat of combustion due to each of the atoms of hydrogen which is linked to a carbon atom, and Σv the total influence that the collective linkages between the atoms of carbon exercise upon the heat of combustion. On resolving Σv into its separate terms, the equation assumes the following form (see p. 386) :—

$$fC_aH_{2b} = \begin{cases} a(x - 2v_1) + b(2y + v_1) \\ + p_2(2v_1 - v_2) + p_3(3v_1 - v_3), \end{cases} \quad . \quad (2)$$

in which v_1, v_2, and v_3 represent the influence exercised upon the heat of combustion by one or other of the three kinds of linkages between the carbon atoms; p_2 and p_3 express the number of double and triple linkages. We can derive the following values from the heats of combustion at constant volume of the aliphatic hydrocarbons:—

$(x - 2v_1) = 105{\cdot}92$ Cal. $\quad (2v_1 - v_2) = 16{\cdot}15$ Cal.
$(2y + v_1) = 52{\cdot}40$ „ $\quad (3v_1 - v_3) = 44{\cdot}37$ „

and when these values are substituted in the preceding equation, we find

$$fC_aH_{2b} = a \times 105{\cdot}92 + b \times 52{\cdot}40 + p_2 \times 16{\cdot}15 + p_3 \times 44{\cdot}37 \text{ Cal.} \quad (3)$$

5. Thermochemical constants.—The heat of combustion, x, of a carbon atom in a gaseous compound can, from what has been said above, be expressed in three ways, which are dependent upon the three kinds of linkages, namely—

$x = 105{\cdot}92$ Cal. $+ 2v_1$
$x = 122{\cdot}07$ „ $+ v_2$
$x = 135{\cdot}50$ „ $+ \frac{2}{3}v_3$

But the value of x can also be deduced from the heat of combustion of carbon monoxide, which at constant volume amounts to 67·67 Cal. (see p. 382). The one atom of oxygen that carbon monoxide takes up on oxidation is linked to the carbon by two valencies—that is, in the same manner as the oxygen atom already present in the molecule of carbon monoxide. The heat of formation of carbon dioxide must therefore be $2 \times 67{\cdot}67$ or 135·34 Cal., provided always that the carbon atom from which the molecule of carbon dioxide is to be formed is present as the constituent of a gaseous compound; whilst the formation of 1 gram-molecule of carbon dioxide by the combustion of amorphous carbon produces only 96·96 Cal. This difference of 38·38 Cal. must therefore be the amount of heat which is consumed in detaching a gram-atom of carbon from the complex molecule of amorphous carbon and converting it into the gaseous state (see p. 383).

Now, since the direct measurement of the heat of combustion, x, of the gram-atom of carbon gives a value of 135·34

Cal., whilst that derived from the heat of combustion of the hydrocarbons should be 135·50 Cal. $+ \frac{2}{3}v_3$, there is every reason to suppose that the thermal effect corresponding to the so-called triple bond is so small that it may, without producing any sensible error, be taken as equal to zero. According to this assumption we obtain the following *thermal values, corresponding to the different linkages between the carbon atoms of the aliphatic compounds :—*

$$v_1 = 14{\cdot}71 \text{ Cal.} \qquad v_2 = 13{\cdot}27 \text{ Cal.} \qquad v_3 = 0,$$

and, furthermore, for the *heat of combustion of a gram-atom of carbon*, and for that of *two gram-atoms of hydrogen linked to carbon atoms—*

$$x = 135{\cdot}34 \text{ Cal.} \qquad 2y = (52{\cdot}40 \text{ Cal.} - v_1) = 37{\cdot}69 \text{ Cal.}$$

But since the heat of combustion of a gram-molecule of hydrogen at constant volume and with the formation of liquid water is 67·49 Cal., we can therefore arrive at the *thermal value of the linkage of hydrogen to the atoms of carbon.* Thus for every gram-molecule of hydrogen, of which two gram-atoms of hydrogen enter into a gaseous compound, this amounts to

$$2r = 29{\cdot}80 \text{ Cal.} = 2c \,.\, h - h \,.\, h.$$

It is evident from the preceding data that there is no appreciable difference in the strength of the single and double linkages between two atoms of carbon, which amount respectively to 14·71 and 13·27 Cal. per gram-atom, and that this is approximately equal to the strength with which the hydrogen atom is bound to the carbon atom, namely 14·90 Cal.

Once the values of x and y are determined, the heat of combustion of a hydrocarbon becomes, according to equation (1)—

$$f\mathrm{C_aH_{2b}} = a \times 135{\cdot}34 \text{ Cal.} + b \times 37{\cdot}69 \text{ Cal.} - \Sigma v; \quad (4)$$

so that in any given case from the heat of combustion of a compound we can determine the total influence of the collective linkages, as well as their nature and number.

6. Benzene, pyridine, thiophene, and trimethylene.—Applied to the aromatic compounds, equation (4) shows that *benzene does not contain double, but nine single linkages between*

the six carbon atoms. Since the heat of combustion of benzene at constant volume is 797·90 Cal., we have for Σv—

$$\Sigma v = 6 \times 135{\cdot}34 \text{ Cal.} + 3 \times 37{\cdot}69 \text{ Cal.} - 797{\cdot}90 \text{ Cal.} = 127{\cdot}21 \text{ Cal.}$$

But 127·21 Cal. is equal to 9 × 14·14 Cal. The value of the single bonds is therefore but little lower than that found for the aliphatic hydrocarbons, namely 14·71 Cal.; but their number must in every case be nine. The mean value of these linkages, as derived from the heats of combustion of five aromatic compounds, amounts to 14·09 Cal. (see p. 393).

Similar researches on the heats of combustion of pyridine and thiophene lead to the same conclusion, namely, that the *molecules of pyridine and thiophene do not contain double linkages, but that they must be derived from saturated hydrocarbons of the formulæ* C_5H_6 *and* C_4H_6, *with respectively seven and five single linkages between the atoms of carbon* (see pp. 431 and 438).

Trimethylene, C_3H_6, is characterized by the fact that the total value of the linkages between the three gram-atoms of carbon amounts only to 22·11 Cal. If we assume that there are three linkages between the carbon atoms, we have only 7·37 Cal. for each bond—that is, just half the value of 14·71 Cal. found above for the single bond. The heat of combustion at constant volume is 497·98 Cal. (see *Therm. Unters.*, iv. 66), and we thus find that

$$\Sigma v = 3 \times 135{\cdot}34 \text{ Cal.} + 3 \times 37{\cdot}69 \text{ Cal.} - 497{\cdot}98 \text{ Cal.} = 22{\cdot}11 \text{ Cal.}$$

It is evident (*loc. cit.*) that this peculiar behaviour is an actual fact, and not due to any errors, experimental or otherwise, so that it remains as a solitary exception amongst a large number of observations.[1] It is also worthy of note that the heat of combustion of trimethylene at constant volume is one and a half times as large as that of ethylene, namely 497·98 as against 332·19 Cal.

7. The heat of formation of a compound is equal to the difference between the heats of formation of the products of

[1] See A. W. Stewart's *Stereochemistry*, p. 444.

combustion and the heat of combustion of the compound; for example—

$$(C_a, H_{2b}) = a(C, O_2) + b(H_2, O) - f.C_aH_{2b} \quad . \quad (5)$$

But the heat of formation of carbon dioxide—that is to say, the heat of combustion of carbon—is dependent upon the allotropic state of the carbon; for the amorphous variety the value is 96·96 Cal. This magnitude was taken as the basis of the calculations of the heats of formation found in Tables 35 to 44, columns 6 and 7, and which are given both at constant pressure and at constant volume. Thus these values express the thermal effect corresponding to the formation of the compound from hydrogen and amorphous carbon; but in order to decompose the complex molecule of solid carbon and produce therefrom carbon atoms in the same physical condition as that in which they exist in the compounds under consideration, an amount of energy is required which, as has been shown above, amounts to 38·38 Cal. for each gram-atom of carbon liberated from the amorphous substance. If, on the other hand, we wish to give the *absolute heat of formation of the compound*—that is to say, the thermal effect which accompanies the formation of a compound when both it and the constituents from which it is formed are in the same physical condition, that is, when they are all present as gases—we must add to the heats of formation given in the tables a value of 38·38 Cal. for each gram-atom of carbon which enters into the compound. Thus, for example, whilst the heat of formation of 1 gram-molecule of CH_4, starting from amorphous carbon, is calculated in Table 35 as 21·17 Cal.; the absolute heat of formation will be 38·38 Cal. greater, or 59·55 Cal. The magnitudes of the absolute heats of formation of the whole of the compounds investigated are given in the last table (pp. 441, *et seq.*).

8. The absolute heat of formation of a compound is equal to the sum of the thermal values corresponding to the collective linkages between the atoms of the compound. If we retain the symbol (C_a, H_{2b}) for the thermal effect on formation of a compound from amorphous carbon, we can, in order to avoid confusion, represent the absolute heat of

formation by the formula (c_a, H_{2b}), where little c indicates that the compound is assumed to be formed by the union of atoms of gaseous carbon with molecular hydrogen.

Thus the absolute heat of formation of a hydrocarbon can be calculated by means of the following simple equation (see p. 398):—

$$(c_a, H_{2b}) = 2b \,.\, r \times \Sigma v, \quad . \quad . \quad . \quad . \quad (6)$$

in which $2r$ corresponds to the thermal value of the linkages between the two atoms of a molecule of hydrogen and the carbon atoms of the compound, which, in accordance with the experimental results, amounts to $2 \times 14{\cdot}90$ Cal.

Isomeric hydrocarbons will therefore have the same heats of formation unless Σv gives unequal values, which happens when the nature and number of the linkages are different. Thus the heats of formation are the same for the isomeric hydrocarbons of the paraffin series, because the number of linkages between the atoms of carbon is always $2a - b$. On the other hand, the two isomeric hydrocarbons, benzene and dipropargyl, have different heats of formation, since the number and nature of the carbon bonds are different. We thus have—

		Calculated.	Experimental.
Benzene	$(c_6, H_6) = 6r + 9u$	$= 216{\cdot}21$	$216{\cdot}61$ Cal.
Dipropargyl	$(c_6, H_6) = 6r + 3v_1 + 2v_3 = 133{\cdot}53$		$133{\cdot}08$ „

There is therefore a difference of $82{\cdot}68$ Cal. between the heats of formation of these two hydrocarbons.

The molecule of the *polymeric hydrocarbons* can be represented by $n \,.\, C_aH_{2b}$; their heats of formation and combustion are not, however, n times a common constant, for Σv is not a common multiple. In the case of the olefines, the molecules of which can be represented by $a.\ CH_2$, we have—

Heat of formation $\begin{cases} a \times 44{\cdot}51 \text{ Cal.} - (2v_1 - v_2) = a \times 44{\cdot}51 \text{ Cal.} \\ \quad - 16{\cdot}15 \text{ Cal.} \end{cases}$

Heat of combustion $\begin{cases} a \times 158{\cdot}32 \text{ Cal.} + (2v_1 - v_2) = a \times 158{\cdot}32 \\ \quad \text{Cal.} + 16{\cdot}15 \text{ Cal.} \end{cases}$

The small value of $2v_1 - v_2$, as compared with the heat of combustion, accounts for the former assumption, based upon

insufficient evidence, that the heat of combustion of the olefines must be a multiple of a common constant.

9. The influence which the oxygen atoms exercise upon the heat of formation of a molecule differs appreciably according to the manner in which the oxygen atoms are united to the other atoms in the molecule. The following relations are noted in the different series of compounds containing oxygen :—

(*a*) *Ethers.*—The molecule of these compounds is supposed to be built up of two alcohol radicals united by an atom of oxygen, and will therefore contain the C. O. C group. There is an average thermal value of 34·31 Cal., corresponding to the formation of this group of atoms. The magnitude is not a constant one, and appears to be partly dependent upon the number of hydrogen atoms, and this must be taken as an indication that the influence of the oxygen, which is known to have a very great affinity for hydrogen and carbon, extends beyond the immediately adjacent atoms.

Ethylene oxide behaves in a precisely similar manner to the ethers, and must have the formula $H_2C.O.CH_2$ with two free valencies; for the introduction of an atom of oxygen into the molecule of ethylene, in place of the double linkage, corresponds to a thermal effect of 93·98 − 73·47 = 20·51 Cal., whilst the taking up of an atom of oxygen by the ethane molecule in place of the single linkage produces a heat effect of 124·95 − 104·51 = 20·44 Cal. The relation is therefore exactly the same, and, if dimethyl ether has the composition $CH_3.O.CH_3$, *ethylene oxide must be dimethylene ether*, $CH_2.O.CH_2$. The earlier view that ethylene oxide contained a single linkage between the carbon atoms would necessitate a heat of formation greater by 14·71 Cal.; that is to say, about 15 per cent. higher than the experimental value.

(*b*) *Alcohols.*—The oxygen atom in a molecule of alcohol is supposed to be present in the form of hydroxyl linked to a carbon atom, so that the molecule contains the $-\overset{|}{\underset{|}{C}}OH$ group. The thermal effect on formation of this group of atoms is

not the same for the primary, secondary, and tertiary alcohols, being smallest for the primary and greatest for the tertiary alcohols. For the *primary* alcohols, including phenol, the heat of formation of the —COH group averages 44·67 Cal. On the assumption that the alcohol is formed from the corresponding hydrocarbon by the introduction of an atom of oxygen, the thermal effect would be 44·67 − 14·90 Cal., or 29·77 Cal. The constituents of the hydroxyl group are therefore bound to the carbon atom with a strength exactly three times as great as that with which a hydrogen atom is linked to carbon; for $3 \times 14{\cdot}90 = 44{\cdot}70$.

In the case of the *secondary* alcohols, the formation of the —COH group corresponds to a thermal effect of 50·71 Cal., and for the dihydric alcohol, ethylene glycol, it has a precisely similar value, namely $2 \times 50{\cdot}80$ Cal. The *trihydric* alcohol, trimethyl carbinol, on the other hand, has a heat of formation of 60·98 Cal. for its —COH group. This large thermal effect which the oxygen atom produces on formation of the secondary and tertiary alcohols is no doubt due to the more central position occupied in the molecule by the hydroxyl group as compared with the primary alcohols.

(*c*) *The aldehydes*, similarly to the alcohols, contain the COH group; but the heat of formation is far greater, namely 64·88 Cal. In this case, therefore, the oxygen atom must have some function other than that which it has in the alcohols. A study of the influence of oxygen on the heats of formation of the ketones and acids may help to throw light on this difference.

(*d*) *Ketones and fatty acids.*—The molecule of the ketones contains two alcohol radicals united to a C : O group. Of the thermal effect on formation of a ketone, 53·52 Cal. is due to the formation of the C : O group. The molecule of the acids contains the monovalent carboxyl group, the constitution of

which is assumed to be $O:C.OH$; and the thermal value corresponding to the formation of this group was found experimentally to be 119·75 Cal. Now, the thermal effect on formation of the COH group of the aldehydes equals 64·88 Cal., whilst the carbonyl group, CO, of the ketones has a heat of formation of 53·52 Cal. The sum of these two numbers is

$$64{\cdot}88 \text{ Cal.} + 53{\cdot}52 \text{ Cal.} = 118{\cdot}40 \text{ Cal.},$$

whilst the thermal value on formation of the carboxyl group of the acids is 119·75 Cal. These two magnitudes may therefore undoubtedly be taken as equal, and all the more so since two out of the three acids investigated gave values of 118·83 and 118·93 Cal., whilst the third had the higher value of 121·48 Cal.

It follows from the statements above that the COH group of the aldehydes must have the constitution $C.OH$, and that the *aldehydes* are non-saturated compounds with two free valencies, whilst the carbon atom in the COH group of the alcohols does not possess free valencies.

(*e*) *Esters.*—The molecules of these compounds are assumed to be built up of an acid radical and an alcohol radical united by an atom of oxygen. The constitution of methyl acetate will therefore be represented by the formula

$$H_3C—O—C(=O)—CH_3.$$

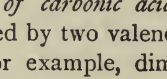
The thermal effect corresponding to the group of atoms

$$C—O—C(=O)—C,$$

amounts, according to Table 50, to 105·44 Cal., as the mean value for five esters. This group contains two atoms of oxygen, each of which is linked to carbon atoms by two valencies. Assuming these valencies to be of equal value, we shall have a thermal effect of $\frac{1}{2} \times 105{\cdot}44$ Cal. for each gram-atom of

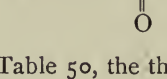
oxygen, or 52·72 Cal., which is in complete agreement with the thermal value found for the ketones, namely 53·52 Cal. for each gram-atom of oxygen united by two valencies to carbon.

In the *esters of carbonic acid* there are three atoms of oxygen, each linked by two valencies to carbon atoms; for the constitution of, for example, dimethyl carbonate can be expressed by the formula



According to Table 50, the thermal value of this group of atoms is 162·44 Cal., or 3 × 54·15 Cal., so that the thermal effect of each of the doubly-linked oxygen atoms is precisely the same as that found for it above.

(*f*) *The anhydrides of the acids* of the paraffin series also contain three atoms of oxygen, each of which is linked by two valencies to carbon; for example, acetic acid anhydride



Unfortunately, I have only investigated this one anhydride, but, of its heat of formation, 165·52 Cal. is due to the formation of the group mentioned above; the value of each gram-atom of oxygen is therefore 55·17 Cal.

We have thus determined the *thermal value of the linkage between the two valencies of an oxygen atom and the carbon atoms* for four series of compounds, and found for the

Ketones	53·52 Cal.
Carbonic esters	54·15 „
Aliphatic esters	52·72 „
Acetic anhydride . . .	55·17 „

As the last value was derived from only a single anhydride, we can place the mean value at 53·46 Cal.

10. Halogen compounds.—*The affinity of chlorine for carbon is approximately equal to that of hydrogen.* This is shown, for

example, by a comparison of the heats of formation of methane and of the chlorides derived from it, which, according to Table 36, are at constant volume—

$$\left.\begin{array}{ll} (C, H_4) & = 21{\cdot}17 \text{ Cal.} \\ (C, H_3, Cl) & = 21{\cdot}97 \quad \text{,,} \\ (C, H, Cl_3) & = 23{\cdot}63 \quad \text{,,} \\ (C, Cl_4) & = 20{\cdot}45 \quad \text{,,} \end{array}\right\} \text{for amorphous carbon.}$$

A further investigation proves (see p. 410) that the thermal effect for the chlorides with two and three atoms of chlorine in the molecule is somewhat higher than for the chlorides with one and four chlorine atoms, and for the corresponding hydrocarbons.

The affinity of chlorine for carbon is greater than that of bromine, whilst iodine has a still smaller value. The thermal values of the linkages between the three substances, in the form of gas or vapour, and carbon is as follows:—

1 gram-atom of	chlorine	and carbon . . .	15·13 Cal.
,, ,,	bromine vapour	and carbon .	7·68 ,,
,, ,,	iodine	,, ,, .	−4·25 ,,

There is therefore a satisfactory agreement between the behaviour of these three elements towards carbon and towards hydrogen (see p. 191).

11. The thermal effect on dissociation of molecules into their atoms shows the following noteworthy relation.—It was demonstrated on p. 382 that the energy which must be supplied to a gram-molecule of amorphous carbon in order to liberate therefrom free gaseous atoms amounts to 38·38 Cal. for each gram-atom of carbon set free. Hence it follows that the maximum thermal value of the linkage between two carbon atoms of a gaseous molecule corresponds to 14·71 Cal. for a single, and to 13·27 Cal. for the so-called double bond.

It follows, from the earlier researches on the heat of dissociation of nitrogen tetroxide, that the splitting up of the gram-molecule of N_2O_4 into two gram-molecules of NO_2 causes an absorption of 13·60 Cal. at constant volume, and this magnitude corresponds to the linkages of the atoms in the *molecule of nitrogen.*

From this value, and the heat of formation of nitric oxide, we can now calculate the thermal effect on dissociation of a *gram-molecule of oxygen*, which amounts to 26·32 Cal., and on comparing this with the value determined by Boltzmann for the heat of dissociation of the *iodine molecule*, namely 27·94 Cal. at constant volume, we obtain the following result :—

$$\begin{aligned} c.c &= \begin{cases} 14{\cdot}71 \text{ Cal.} \\ 13{\cdot}27 \quad \text{„} \end{cases} \\ n.n &= 13{\cdot}02 \quad \text{„} \\ o.o &= 2 \times 13{\cdot}16 \quad \text{„} \\ i.i &= 2 \times 13{\cdot}97 \quad \text{„} \end{aligned}$$

that is to say, the thermal value on dissociation of the molecules of these four elements into their atoms appears to be a multiple of a constant magnitude, equal to approximately 13·70 Cal.

12. A study of the heats of formation of the compounds of nitrogen has led to the following results :—

(*a*) *Nitrogen and carbon have but small affinity one for the other.* The linkage between a gram-atom of carbon and of nitrogen amounts to 2·77 Cal. for each single bond, so that the triple linkage between two dissimilar, polyvalent atoms produces a thermal effect of 8·31 Cal. But since the dissociation of the gram-molecule of nitrogen requires 13·02 Cal., the thermal value given must be diminished by 6·51 Cal. if we suppose the formation of the nitrile to take place from molecular nitrogen.

(*b*) *The nitro-compounds* (nitromethane and nitroethane) *do not contain the NO_2 group.* The high value found for their heats of formation shows that half of the oxygen must be linked to carbon; and the experimental and calculated results are in perfect accordance with the theory that these substances are derivatives of alcohol, in which one of the hydrogen atoms of the alcohol radical is replaced by NO. Thus the formula of nitromethane becomes $HO.CH_2.NO$, and with such a constitution the products of decomposition can be explained in a simple and natural manner (see also p. 432).

(*c*) *The heats of formation of the amines point to a difference*

in constitution between the aliphatic and the aromatic series. It is found as the result of experiment that the primary aromatic amines, and similarly also allylamine and piperidine, must have the constitution $R . NH_2$; but the primary aliphatic amines are of a different constitution, for they must be regarded as addition products of ammonia and of a divalent alkylene radical, for example, $CH_2 : NH_3$. Thus the heat of formation of methylamine, in accordance with the experimental results, is equal to the sum of the heats of formation of methylene and of ammonia, together with the thermal value of the double linkage between carbon and the nitrogen atom. The nitrogen atom is therefore in this case pentavalent, as it also is in the corresponding secondary and tertiary amines, such as, for example, $CH_3 . NH_2 : CH_2$ and $2(CH_3) : NH : CH_2$.

The heats of formation of the primary amines are higher than those of their secondary and tertiary isomers, and this also is in agreement with the different linkages of the atoms.

That *pyridine* and *piperidine* do not contain double linkages between the carbon atoms, but are derived from the saturated hydrocarbons C_5H_6 and C_5H_{10}, with respectively seven and five linkages, is also a natural conclusion from their heats of formation (see p. 431).

13. Compounds of sulphur.—It has been experimentally shown that the atoms of carbon and sulphur in the mercaptans and sulphides are only very feebly bound; indeed, the thermal effect is negative for molecular sulphur. On the other hand, the value of the linkages of the carbon and sulphur atoms is considerably greater in carbon disulphide and carbonyl sulphide.

In the case of *thiophene*, the heat of formation leads to the conclusion that its molecule corresponds to a saturated hydrocarbon, C_4H_6, in which the carbon atoms are united by five single linkages, and in which two atoms of hydrogen are replaced by an atom of sulphur (see p. 437).

CHAPTER XVI

FORMATION AND DECOMPOSITION OF ORGANIC COMPOUNDS REGARDED FROM THE DYNAMICAL STANDPOINT

THE results of my numerous experimental determinations of the thermal effect on formation of organic compounds from their elements afford abundant material in illustration of the principles underlying chemical reactions which were laid down in a preceding chapter (see p. 333). Since the thermal values were always determined for the same state of aggregation, namely, the gaseous, and since the majority of the reactions in which organic substances are formed or decomposed must be carried out at comparatively low temperatures, because the substances will not as a rule stand strong heating, *the reactions will result in an evolution of heat as an expression of the saturation of the strongest affinities.*

It is this property which we shall now proceed to illustrate by means of numerous examples drawn from the material in question. We shall make use of the numbers given in the fourth column of the tables on pp. 441, *et seq.*, which represent the heats of formation at constant volume; that is to say, when the reacting constituents and the substances formed occupy the same volume, these values being calculated from the heats of combustion (see p. 368). The values are therefore valid for substances in the state of gas or vapour at approximately 18°, and for the formation with *amorphous carbon* as the starting-point. The unit is in all cases the kilogram-calorie.

1. The action of chlorine, bromine, or iodine upon saturated hydrocarbons.—When chlorine is substituted in

a hydrocarbon with the formation of hydrogen chloride we have the following reaction :—

$$C_aH_{2b} + Cl_2 = C_aH_{2b-1}Cl + HCl.$$

The corresponding thermal effect will be, for example, for methane

$$(C, H_3, Cl) + (H, Cl) - (C, H_4) = Q$$
$$21{\cdot}97 \quad + \quad 22{\cdot}00 \quad - \quad 21{\cdot}17 \quad = 22{\cdot}80 \text{ Cal.}$$

Thus the process takes place with an evolution of 22·80 Cal., and the heats of reaction of all the saturated hydrocarbons are of about this same value. For instance, for benzene

$$(C_6, H_5, Cl) + (H, Cl) - (C_6, H_6) = Q$$
$$-12{\cdot}38 \quad + \quad 22{\cdot}00 \quad + \quad 13{\cdot}67 \quad = 23{\cdot}29 \text{ Cal.}$$

By the further action of chlorine upon a chloride the substitution can go further; thus chloroform is formed from methyl chloride and chlorine according to the following reaction :—

$$CH_3Cl + 2Cl_2 = CHCl_3 + 2HCl,$$

and the thermal effect will therefore be

$$(C, H, Cl_3) + 2(H, Cl) - (C, H_3, Cl) = Q$$
$$23{\cdot}53 \quad + \quad 44{\cdot}00 \quad - \quad 21{\cdot}97 \quad = 2 \times 22{\cdot}78 \text{ Cal.}$$

and so on. The thermal effect in all such substitutions is approximately equal for each molecule of chlorine.

Benzene and chlorine can also form *addition compounds;* for example, $C_6H_6Cl_6$. The formation of such compounds is attended by the breaking of one of the nine linkages of the benzene for each molecule of chlorine taken up. Now, the linkage between chlorine and carbon corresponds to about 30·00 Cal. for each gram-molecule of Cl_2, whilst the carbon bonds in benzene have a value of 14·09 Cal.; the addition of 3 gram-molecules of chlorine is therefore accompanied by an evolution of

$$3(30{\cdot}00 - 14{\cdot}09) = 47{\cdot}73 \text{ Cal.}$$

HCl is again formed. In the form of an equation, this can be expressed as follows:—

$$(C, H_3, Cl) + (H, Cl) - (C, H_4) = A$$
$$-(C, H_3, Cl) + (H, Cl) + (C, H_4) = B$$

so that $A + B = 2(H, Cl)$; that is to say, equals 44·00 Cal.

When either bromine or iodine is taken up instead of chlorine, the sum of these thermal values will be respectively $2 \times 11{\cdot}72$ Cal. and $-2 \times 0{\cdot}62$ Cal., which are the heats of formation of 2 gram-molecules of HBr and HI. In the table below the thermal values of the two processes are compared in the case of the methyl and ethyl compounds; A corresponds to the action of the halogen upon the hydrocarbons, B to the action of hydrogen upon the halides.

		A	B	$A+B$
Chlorine	Methyl	22·80	21·20	44·00 Cal. = 2(H, Cl)
	Ethyl	24·15	19·85	
Bromine	Methyl	4·76	18·68	23·44 „ = 2(H, Br)
	Ethyl	6·16	17·28	
Iodine	Methyl	−18·94	+17·70	− 1·24 „ = 2(H, I)
	Ethyl	−18·08	+16·84	

The thermal value B—that is to say, that due to the reduction of the halide by means of hydrogen—is approximately equal for the three halogens, and the reduction also takes place readily in every instance. On the other hand, the value A shows considerable differences, in accordance with the well-known fact that hydrocarbons are readily attacked by chlorine, with greater difficulty by bromine, but are not acted upon at all by iodine.

4. Decomposition of halogen compounds by means of alkalies.—The non-saturated hydrocarbons are able to unite directly with hydrochloric, hydrobromic, and hydriodic acids. The reaction goes slowly with hydrochloric acid, and most readily with hydriodic acid, notwithstanding that in all three cases the action of the halogen acid is attended by an approximately equal evolution of heat; for example, in the case of ethylene and hydrobromic acid—

$$(C_2H_4, HBr) = (C_2, H_5, Br) - (C_2, H_4) - (H, Br) = 12{\cdot}87 \text{ Cal.}$$

The thermal effect for the hydrocarbons with triple linkages will, of course, be some 13 Cal. greater.

The opposite process, namely, the decomposition of a halogen compound with the formation of hydrogen chloride, will therefore be attended by an absorption of heat; for example, the decomposition of ethylene chloride into vinyl chloride and hydrogen chloride will correspond to a thermal value—

$$(C_2, H_3, Cl) + (H, Cl) - (C_2, H_4, Cl_2) = Q$$
$$-2{\cdot}46 \quad + \quad 22{\cdot}00 \quad - \quad 33{\cdot}12 \quad = -13{\cdot}58 \text{ Cal.}$$

The reaction takes place only under the influence of some external agency, and is usually brought about by warming ethylene chloride with a solution of caustic potash. The resulting evolution of heat is due to the energy of the reaction between hydrochloric acid and the base, and, when caustic potash is used, it amounts to over 31 Cal.

Bromine and iodine compounds behave in precisely the same manner as chlorine compounds with respect to caustic potash, and the resulting thermal effect of the reactions is approximately the same in all three cases.

The addition of a halogen to a non-saturated hydrocarbon, with subsequent separation of the hydrogen halide, is known to be extensively used in chemical synthesis. For instance, in this manner were formed the series of compounds: C_2H_4—$C_2H_4Cl_2$—C_2H_3Cl—$C_2H_3Cl_3$—$C_2H_2Cl_2$—$C_2H_2Cl_4$—C_2HCl_5—C_2Cl_4, likewise $C_3H_5 . OH$—$C_3H_5Br_2OH$—$C_3H_3 . OH$, and so on. All these processes take place with evolution of heat, the magnitude of which is approximately equal to that mentioned above.

5. The formation of alkyl halides from alcohol, and conversely of alcohols from the corresponding halogen compounds.—The halides of the alkyl radicals are usually prepared by the action of the phosphorus halides upon the alcohol, when a considerable evolution of heat at once becomes apparent. But the hydrogen halides also react with alcohol with evolution of heat; for example, with ethyl alcohol and hydrogen chloride we have

$$(C_2, H_5, Cl) + (H_2, O) - (C_2, H_6, O) - (H, Cl = Q$$
$$29{\cdot}55 \quad + \quad 57{\cdot}64 \quad - \quad 57{\cdot}02 \quad - \quad 22{\cdot}00 = 8{\cdot}17 \text{ Cal.}$$

HCl is again formed. In the form of an equation, this can be expressed as follows:—

$$(C, H_3, Cl) + (H, Cl) - (C, H_4) = A$$
$$-(C, H_3, Cl) + (H, Cl) + (C, H_4) = B$$

so that $A + B = 2(H, Cl)$; that is to say, equals 44·00 Cal.

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$$-2{\cdot}46 \quad + \quad 22{\cdot}00 \quad - \quad 33{\cdot}12 \quad = -13{\cdot}58 \text{ Cal.}$$

The reaction takes place only under the influence of some external agency, and is usually brought about by warming ethylene chloride with a solution of caustic potash. The resulting evolution of heat is due to the energy of the reaction between hydrochloric acid and the base, and, when caustic potash is used, it amounts to over 31 Cal.

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$$(C_2, H_5, Cl) + (H_2, O) - (C_2, H_6, O) - (H, Cl = Q$$
$$29{\cdot}55 \quad + \quad 57{\cdot}64 \quad - \quad 57{\cdot}02 \quad - \quad 22{\cdot}00 = 8{\cdot}17 \text{ Cal.}$$

The reaction is here supposed to take place between the substances in the state of gas or vapour, so that the heat of formation of the water is given as 57·64 Cal.; the value holds good for water vapour at 18° and at constant volume.

In the series of alcohols corresponding to the fatty acids, the thermal effect rises somewhat with an increase of molecular weight, since the heat of formation of the chlorides does not run parallel with that of the alcohols. For allyl alcohol and hydrogen chloride the thermal effect equals 11·83 Cal., for phenol 6·63 Cal. Hydrogen bromide and hydrogen iodide behave in a similar manner in the presence of alcohol, only that the thermal effect is some 2 to 3 Cal. higher than in the case of hydrogen chloride (see also *Therm. Unters.*, iv. p. 376).

The reverse process, namely, the conversion of a halogen compound into an alcohol, may be brought about either directly by the action of potassium hydroxide upon the halide, or indirectly by first treating the halogen compound with potassium acetate, and then decomposing the alkyl acetate formed by means of potassium hydroxide. Since, however, the potassium acetate is first decomposed, and then again re-formed, its participation in the process exercises no influence on the thermal value of the main reaction—that is, in the conversion of the halogen compound into an alcohol. But the action of the hydrogen halides upon the alcohols is attended by an evolution of heat; the reverse process will therefore naturally correspond to an absorption of heat. But, as we saw in a preceding example (see p. 464), the energy of the reaction between the hydrogen halides and potassium hydroxide is sufficient to cause the total reaction to result in an evolution of heat. The fact that the iodides of the tertiary alcohols can be hydrolyzed by water (without the co-operation of an alkali) is due to the heats of formation of these alcohols being about 17 Cal. higher than those of the corresponding primary alcohols, so that this process also takes place with evolution of heat.

The formation of an alcohol by the action of silver oxide (or lead oxide) and water upon the corresponding halide is likewise attended by a considerable evolution of heat. Curiously enough, however, the reaction goes more readily with the

bromine and iodine compounds than with the chlorine compound, notwithstanding that the thermal effect is in all three cases approximately the same and of considerable magnitude. In a like manner the formation of ethylene glycol from ethylene chloride, silver oxide, and water is accompanied by an evolution of 50·53 Cal.; we thus have

$$(C_2, H_6, O_2)+(Ag_2, Cl_2)-(C_2, H_4, Cl_2)-(Ag_2, O)-(H_2, O)=Q$$
$$99{\cdot}15 + 58{\cdot}76 - 33{\cdot}12 - 5{\cdot}90 - 68{\cdot}36 = 50{\cdot}53 \text{ Cal.}$$

and an equally noticeable thermal effect is also observed in certain other cases when silver oxide is employed in the reduction of halogen compounds.

6. Decomposition of alcohols with the separation of water.—When the non-saturated hydrocarbons are able to form alcohols by the addition of water, the thermal value of the process, provided all the substances are assumed to be present in the form of gas or vapour, will have the values represented by Q in the table below.

Alcohol.	Heat of formation.		$Q = A -$ (B + 57·64 Cal.).
	A: Alcohol, $C_aH_{2a}+{}_2O$	B: Hydrocarbon, C_aH_{2a}	
Ethyl alcohol . .	57·02 Cal.	−3·29 Cal.	2·67 Cal.
Propyl alcohol. .	63·66 ,,	+2·06 ,,	3·96 ,,
Isopropyl alcohol .	68·97 ,,	2·06 ,,	9·27 ,,
Trimethyl carbinol	85·69 ,,	8·92 ,,	19·13 ,,

If from the heat of formation of the alcohol we deduct the sum of the heats of formation of the hydrocarbon and of water-vapour, we obtain the values given under Q, all of which are positive. The process is brought about by means of concentrated sulphuric acid and final dilution with water; but it will even take place with evolution of heat without dilution, provided it is able to take place at all.

The reverse process, namely, *the decomposition of an alcohol to form a hydrocarbon and water*, will naturally be attended by an absorption of heat equal to $-Q$. But this process also is brought about by the addition of concentrated sulphuric acid,

and the strong affinity of the acid for the water formed provides sufficient energy for the process to result in an evolution of heat.

The ethers can likewise be formed by the interaction of sulphuric acid and alcohol when mixed in suitable proportions. If the reaction is properly carried out, the thermal effect will be in accordance with the equation below, which represents the formation of 1 gram-molecule of dimethyl ether and 1 gram-molecule of water by the decomposition of 2 gram-molecules of methyl alcohol—

$$(C_2, H_6, O) + (H_2, O) - 2(C, H_4, O) = Q$$
$$48{\cdot}19 + 57{\cdot}64 - 2 \times 50{\cdot}58 = 4{\cdot}67 \text{ Cal.}$$

The process therefore results in an evolution of heat. That this must also be the case on formation of other ethers and esters by removal of water from the corresponding alcohols is evident from the figures in the table below, where Q represents the thermal effect of the reaction.

Ether.	Heat of formation.		$Q = A - (B + 57{\cdot}64$ Cal.).
	A : of the two alcohols.	B : of the ether.	
Dimethyl ether . .	50·58 + 50·58 Cal.	48·19 Cal.	4·67 Cal.
Methylethyl ether .	50·58 + 57·02 ,,	56·42 ,,	6·46 ,,
Diethyl ether . .	57·02 + 57·02 ,,	67·43 ,,	11·03 ,,
Methylallyl ether .	50·58 + 29·75 ,,	32·05 ,,	9·36 ,,
Diallyl ether . .	29·75 + 29·75 ,,	9·85 ,,	7·99 ,,
Methylphenyl ether	50·58 + 16·63 ,,	13·83 ,,	4·26 ,,
Dimethylene ether (Ethylene oxide)	Ethylene glycol 99·15 ,,	17·22 ,,	−24·29 ,,

The reaction does not take place spontaneously, but requires a catalyzer, which, however, exercises no influence on the thermal value.

Ethylene oxide.—The dihydric alcohol, ethylene glycol, behaves quite differently from the monohydric alcohols. This was already apparent from the negative value of Q, which is so considerable that it is not even compensated by the affinity of sulphuric acid for water. Nor does the action of sulphuric acid upon ethylene glycol give rise to ethylene oxide, but to *ethyl*

aldehyde, the heat of formation of which is 30·65 Cal. greater than that of ethylene oxide; so that the process, even without the action of the sulphuric acid, takes place with evolution of heat.

Concurring with this is the *power that ethylene oxide has to unite directly with water* to form glycol with an evolution of 24·29 Cal., whilst the other ethers do not take up water, since the process would be attended by absorption of heat.

Acetic anhydride.—Whilst the anhydrides of the monohydric alcohols are not hydrolysed by water, the corresponding acid anhydrides, on the other hand, are directly decomposed by 1 gram-molecule of water to form 2 gram-molecules of the acid. The reaction proceeds with evolution of heat, which, in the case of acetic anhydride, amounts to 19·80 Cal., as calculated for the substances in the state of vapour.

7. Formation of esters.—The alkyl halides react, as is well known, with silver salts to form an ester and the silver halide. This reaction is employed in the formation of the esters of carbonic acid, and proceeds with a considerable evolution of heat. Thus the preparation of *dimethyl carbonate* and of *diethyl carbonate* from the iodides, by their action upon silver carbonate, takes place with an evolution of respectively 46·51 and 45·29 Cal.

The alkyl isocyanides (carbylamines) can be prepared in the same manner, and the reaction proceeds with an evolution of 16·68 Cal. The reason that these substances cannot be formed by the general method used for the preparation of the majority of esters and halogen derivatives, as, for example, by heating a potassium alkyl sulphate with potassium cyanide, which, in the case in question, would give rise to a nitrile, must be due to the fact that the *heat of formation of the nitriles is some* 14·90 *Cal. greater than that of the isomeric isocyanides.* Owing to this property the isocyanide formed is gradually converted into a nitrile, and the conversion will be attended by the evolution of an additional 14·90 Cal.

Alcohols and organic acids can undergo mutual decomposition with the formation of an ester and of water, but the conversion is only partial, since the water formed by diluting

the reacting substances weakens their action. On the other hand, if the water formed be removed by means of some desiccating agent, such as concentrated sulphuric acid, zinc chloride, calcium chloride, or similar substances, the reaction proceeds to an end. If we calculate the thermal effect consequent upon the reaction between the acid and alcohol in the state of vapour, we shall obtain a negative value; but if, on the other hand, the reaction is between the liquid substances, there will be a small evolution of heat. The part played by the desiccating agent can be illustrated by the following simple lecture experiment: anhydrous methyl alcohol and formic acid are mixed in equivalent proportions, when an almost inappreciable partial reaction occurs; if now the mixture be poured on to some granular calcium chloride the reaction proceeds with great rapidity, and, as a result of the heat thereby evolved, the methyl formate distils over in a state of almost chemical purity.

8. Oxidation products of the alcohols.—The primary alcohols on oxidation give rise to aldehydes, the secondary alcohols to ketones; and both processes result in evolution of heat. The differences between the heats of formation of the alcohols and of the aldehydes are shown by the experimental results contained in the following table:—

	Ethyl-	Propyl-	Isobutyl-
Alcohol	57·02	63·66	68·54 Cal.
Aldehyde	47·87	53·79	59·31 „
Difference	9·15	9·87	9·23 Cal.

The mean difference is 9·42 Cal. Now, since on oxidation of an alcohol, in addition to the aldehyde, there is also formed a molecule of water, the heat of formation of which (in the state of vapour) is 57·64 Cal. per gram-molecule, the average thermal value on oxidation of an alcohol to an aldehyde will be

$$(C_aH_{2b}O : O) = 57{\cdot}64 - 9{\cdot}42 = 48{\cdot}22 \text{ Cal.}$$

In a similar manner we can find the thermal effect on oxidation of the secondary alcohols to ketones from a

knowledge of the heats of formation of these latter and of those of the alcohols, which are given in the following table:—

	Isopropyl-	Dimethylethyl-
Alcohol	68·97	81·32 Cal.
Ketone	57·26	69·40 „
Difference . . .	11·71	11·92 Cal.

The heats of oxidation are therefore somewhat lower on formation of the ketone than on formation of the aldehyde, namely—

$$57{\cdot}64 - 11{\cdot}82 = 45{\cdot}82 \text{ Cal.}$$

On oxidation of an aldehyde one atom of oxygen is taken up and an acid is formed. The thermal effect is given by the difference between the heats of formation of the two compounds; thus for

$$\left.\begin{matrix}\text{Acetic acid} - \text{acetic} \\ \text{aldehyde}\end{matrix}\right\} = 104{\cdot}13 - 47{\cdot}87 = 56{\cdot}26 \text{ Cal.}$$

$$\left.\begin{matrix}\text{Propionic acid} - \text{pro-} \\ \text{pionic aldehyde}\end{matrix}\right\} = 107{\cdot}71 - 53{\cdot}79 = 53{\cdot}92 \text{ „}$$

The average heat of oxidation therefore amounts to 55·09 Cal.; and this high value explains the strong reducing action of the aldehydes.

9. Decomposition of acids and their salts with separation of carbon dioxide and the formation of hydrocarbons, aldehydes, and ketones.—Many acids or their salts are decomposed on heating with the separation of carbon dioxide; thus phthalic acid on heating is converted into benzoic acid, and this again into benzene; oxalic acid gives rise to formic acid, which latter splits off hydrogen.

The thermal effect of the above-mentioned processes is equal to the difference between the heats of formation of the products of the decomposition and of those of the acids concerned, and must naturally be calculated for all of the substances in the same state of aggregation, for otherwise the results would be influenced by the heats of fusion or of vaporization. Thus, for example, the thermal value of the splitting up of oxalic acid into carbon dioxide and formic acid is found to be

$-8{\cdot}49$ Cal. when we subtract 200·80 Cal., which is the heat of formation at constant volume of solid oxalic acid, from the sum of the heats of formation in the gaseous state of carbon dioxide and formic acid (96·96 and 95·35 Cal.); but the true value will be found only when the heat of vaporization of oxalic acid is added on to the above-mentioned $-8{\cdot}49$ Cal., and then the result would undoubtedly become positive.

(*a*) *Formation of hydrocarbons.*—When a fatty acid splits up in accordance with the equation

$$C_{a+1}H_{2a+2}O_2 = CO_2 + C_aH_{2a+2},$$

there will be formed, for instance, in the cases of formic, acetic, and propionic acids, hydrogen, methane, and ethane respectively, in addition to carbon dioxide. The thermal effect, Q, of such a process will therefore be equal to the difference between the sum of the heats of formation of carbon dioxide and of the hydrocarbon and of that of the acid; these values are given in the table below.

Acid.	Heat of formation, p, of the			Q
	Acid.	Carbon dioxide.	Hydrocarbon.	
Formic acid .	95·35 Cal.	96·96 Cal.	—	1·61 Cal.
Acetic acid . .	104·13 ,,	96·96 ,,	21·17 Cal.	14·00 ,,
Propionic acid .	107·71 ,,	96·96 ,,	27·40 ,,	16·65 ,,

The reaction will consequently take place with evolution of heat. The great difference between the heats of formation of formic acid and of the other two acids is not accidental, nor due to any inaccuracy, but arises from the fact that in the reaction with formic acid it is hydrogen which is separated, but with the other two acids a hydrocarbon. Hence it follows that whilst the thermal effect for the last two acids must be approximately equal, that of formic acid will be $2r - v_1$ less; and this difference amounts to about 15 Cal., and is thus in agreement with the value found for Q.

In the presence of finely divided platinum the vapour of *formic acid* is extremely easily decomposed into carbon dioxide

and hydrogen at the boiling-point of the acid. The other acids are decomposed less readily and completely on heating; but the process can usually be effected by heating the sodium salt of the acid with sodium hydroxide, when sodium carbonate and a hydrocarbon are formed. The thermal value of the last reaction is some 10 Cal. greater than on decomposition of the free acid, and the reaction goes readily and proceeds to an end.

(*b*) *Formation of ketones.*—The fatty acids can also be decomposed to ketones, water, and carbon dioxide. Provided the decomposition of the acids, in the state of vapour, were to take place spontaneously, the process would be represented by

$$2C_2H_4O_2 = CO_2 + H_2O + C_3H_6O,$$

which corresponds to a thermal effect

$$(C, O_2) + (H_2, O) + (C_3, H_6, O) - 2(C_2, H_4, O_2) = Q$$
$$96{\cdot}96 + 57{\cdot}64 + 57{\cdot}26 - 2 \times 104{\cdot}13 = 3{\cdot}60 \text{ Cal.}$$

The thermal value of the corresponding decomposition of propionic acid is 8·58 Cal. The process is not, however, carried out with the acids themselves, but by heating their sodium or calcium salts, and by this means the thermal effect is still further augmented.

(*c*) *The formation of aldehydes* takes place on heating the sodium salt of an acid with sodium formate, whereby sodium carbonate and the aldehyde are formed. If the process is carried out with the free acid in the state of vapour, it will be expressed by the equation

$$CH_3 . COOH + H . COOH = CO_2 + H_2O + C_2H_4O,$$

and will be attended by the following thermal effect:—

$$(C, O_2) + [H_2, O] + (C_2, H_4, O) - (C, H_2, O_2) - (C_2, H_4, O_2) = Q$$
$$96{\cdot}96 + 57{\cdot}64 + 47{\cdot}87 - 95{\cdot}35 - 104{\cdot}13 = 2{\cdot}99 \text{ Cal.}$$

A similar decomposition of propionic acid will produce a thermal effect of 5·27 Cal. The process therefore proceeds with evolution of heat, but, as mentioned above, it is brought about by means of the sodium salt, and in this manner the

reaction takes place readily and with a somewhat greater evolution of heat.

The preceding examples, which might easily be multiplied in number, serve to illustrate the reactions in which organic compounds are formed or transformed. In every case when the reaction is attended by an evolution of heat, it is an indication of the saturation of the strongest affinities. The relation is the same as that which I have shown to exist in the reactions between inorganic substances (pp. 330 to 363), namely, that chemical reactions are based upon the tendency of the atoms to attain a state of more stable equilibrium, a tendency which can be satisfied when the conditions mentioned on p. 333 are fulfilled. The reaction can then take place, and will proceed with a liberation of energy, which usually manifests itself in the form of heat.

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